

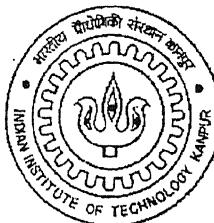
Oxidative Dehydrogenation of Propane Over Modified Cr₂O₃/ Al₂O₃ and Cr₂O₃/ TiO₂ Catalysts: Effect of Vanadium and Sodium

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Requirements for the Degree of
Master of Technology*

S. S. B.

by

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to the
Department of Chemical Engineering
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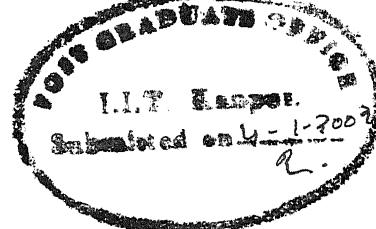
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CERTIFICATE



It is certified that the work contained in the thesis entitled **Oxidative Dehydrogenation of Propane Over Modified Cr₂O₃/ Al₂O₃ and Cr₂O₃/ TiO₂ Catalysts: Effect of Vanadium and Sodium** by *Rohit Gupta* has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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Abstract

Two sets of sodium and vanadium oxide modified 5% Cr₂O₃/Al₂O₃ and 1% Cr₂O₃/ TiO₂ catalysts were prepared using incipient wetness impregnation method and characterized by various techniques. The modified catalysts were characterized using Raman spectroscopy, XRD analysis, EPR spectroscopy and TPR studies. The reactivity of the catalysts were tested for their reactivity in the oxidative dehydrogenation (ODH) of propane. XRD analysis reveals that no new compounds are formed on the catalysts due to the presence of additives. EPR results show the presence of Cr⁵⁺ species in both series of catalysts. However, Cr⁵⁺ species appears to be chemically inactive for the ODH of propane. Raman and TPR studies revealed that vanadium oxide coordinate directly to the oxide support, without significantly interacting with the surface chromium oxide species. The addition of vanadium oxide increased the propane conversion and propene selectivity. The increased activity and selectivity is explained by the combined effect of both surface active species, chromium and vanadium oxide. Sodium directly coordinates with the surface chromium oxide species and increases the reducibility (T_{max} temperature) and decreases the reduction degree (H/Cr ratio). This is also reflected in the decrease in activity and selectivity for sodium modified catalysts. Consequently, sodium behaves as an interacting additive by poisoning the surface chromium oxide site and vanadium behaves as a non-interacting additive since the vanadium and chromium oxide surface sites appear to co-exist independent of the other.

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Chapter 1

Introduction

1.1 Supported Metal Oxide Catalysts

Heterogeneous catalysis has become the basis of industrial and environmental chemistry during this century due to the fundamentals being developed with ever increasing speed [1]. Among different heterogeneous catalysis systems supported metal oxide catalysts constitute an important class due to its various industrial application [2].

Supported metal oxides are formed when one metal oxide (i.e., Cr_2O_3 , Re_2O_7 , V_2O_5 , etc.), the supported metal oxide phase, is deposited on a second metal oxide substrate (i.e. Al_2O_3 , TiO_2 , SiO_2 , etc), the oxide support that usually possesses high surface area [3]. The supported metal oxide phase is present on the oxide support as a surface metal oxide species and this is considered to be the active phase of the catalyst. Previous studies dealing with supported metal oxide catalysts have shown that the nature of the surface metal oxide species depends on the oxide support, metal oxide loading, preparation method, and the presence of additives [4].

1.2 Uses of Supported Chromium Oxide Catalyst

Supported chromium oxide forms a specific example of supported metal oxide catalysts. The activity and selectivity of chromium oxide supported catalysts in alkane dehydrogenation has been known for several decades [5]. Other industrial applications of supported chromium oxide catalysts are in hydrogenation and polymerization reactions. Apart from these applications, supported chromium oxide catalysts are also used for the decomposition of H_2O_2 , the oxidation of CO , the exchange of H_2 and D_2 and the

hydrochloronation of propene [6]. Due to the various applications of supported chromium oxide catalysts they have studied extensively by various research groups.

1.3 Effect of Additives

Supported chromium oxide catalysts typically used in industry and research usually contain various additives (impurities and promoter) that are intentionally or unintentionally added. The oxides of alkali metals (Na, K, Li.etc.), and oxides of tungsten, niobium, vanadium are some of the main additives usually considered for supported chromium oxide catalysts [21]. Additions of vanadium or tungsten oxide increase the activity of certain reaction [20], whereas potassium, sodium and phosphorus oxides are considered poison for certain reactions. In some cases, the above additives decrease the activity but increase the selectivity for the particular reaction [21]. In essence, some of these additives are detrimental to the catalytic oxidation properties, where as others are necessary to obtain maximum catalytic efficiency. Furthermore, only a critical amount of additive is usually necessary to form the active catalysts.

1.4 Catalyst characterization

In order to better understand how a heterogeneous catalysts function, many different characterization techniques have been applied to obtain the fundamental information about the bulk and surface properties of catalytic materials.

These characterization techniques are used to study the nature of the surface species.

Only a handful of spectroscopic characterization methods are able to provide *insitu* molecular level analysis. Some of the common techniques applied to supported metal oxide catalysts are IR, Raman, UV-vis, NMR and EPR spectroscopy.

Raman spectroscopy

This technique is best suited to identify the molecular structure of supported metal oxide

catalysts. It can readily discriminate between the different molecular states of supported metal oxides. Each state possesses a unique spectrum that is related to its structure [7]. Therefore, Raman studies provide direct information about the structure of each state and method of discriminate between different molecular states.

X-ray diffraction (XRD)

It is simple and reliable technique to know the specific phases present in samples and estimating the particle size. Solid phases in a catalyst are identified by their characteristic diffraction pattern. However, amorphous or bulk oxide or mixed oxide phase of small crystalline size are not readily identified by XRD.

Electron paramagnetic resonance spectroscopy (EPR)

The EPR technique is extensively used to study the paramagnetic species that exist on various solid surfaces. These species may be supported metal ions, surface defects, or adsorbed molecules, ions etc. Each surface entity must have one or more unpaired electron.

Temperature programmed reduction (TPR)

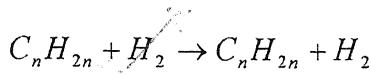
TPR with hydrogen is a widely used technique for the characterization of reducible solids and catalysts. It is used for the identification of phases in supported catalysts precursors. Catalysts that undergo reduction during their catalytic cycle are ideally studied by TPR. TPR studies also provide the extent of reduction of a catalyst.

1.5 Oxidative Dehydrogenation (ODH) of Light Alkanes

Catalytic ODH of light alkanes to alkenes is a challenging problem. In principle it offers a much-needed alternative to pyrolysis and dehydrogenation as a route for the production of alkenes and intermediate chemicals in the petrochemical industry. This is a particularly useful route due to the abundant supplies of liquefied petroleum gas (LPG), which

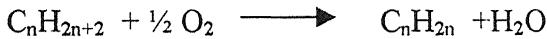
predominantly contains propane and butane [8].

The dehydrogenation reaction of alkanes can be represented as:



In dehydrogenation process the removal of hydrogen requires the breaking of C-H bond, which in turn requires high thermal energy, due to the endothermicity of the reaction ($\Delta H^\circ = 133 \text{ KJ/mol}$). Catalytic dehydrogenation reaction at such high temperature has a number of disadvantages. At high temperature, undesired side reactions take place that are difficult to control. Cracking of alkane is one of the most undesirable side reaction that occurs. It leads to the formation of coke on the catalysts. Being a highly endothermic reaction, heat must also be added to sustain the reaction. Dehydrogenation reactions also occur at low partial pressure of propane ($\Delta G^\circ = 0$ at 767°C), which requires a very large reactor to give reasonable rate of production.

The catalytic ODH of hydrocarbons offers a promising alternative to ← pyrolysis and catalytic dehydrogenation. The overall reaction is represented as



The formation of a very stable product, water, makes this reaction thermodynamically favorable. Theoretically complete conversion can be obtained even at low temperature and high pressure. This provides great advantage over the catalytic dehydrogenation process based on engineering and economic consideration. Furthermore, the ODH reaction is exothermic reaction, which helps to keep it self sustained and heat need not be supplied. However, due to the presence of oxygen there are many other reactions possible like formation of oxygenates, such as aldehyde, ketone, acids [7]. Total combustion of alkanes to carbon dioxide is also possible. In most cases these side-reactions are more

favored then the desired ODH reaction. Thus, the ODH reaction provides a viable alternative to produce olefins but requires a selective catalyst to produce a desired product and eliminate the side reaction.

1.6 Literature Review

A brief literature review of the influence of additives on supported metal oxides in general and supported chromium oxide in particular is given below. This literature review also contains the ODH of alkanes studies over various supported metal oxide catalysts since this is the reaction under consideration in the present work.

Hardcastle & Wachs [9] examined low coverage (0.5-5.0%) of $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts by means of Raman spectroscopy under ambient conditions. These authors reported that alumina support stabilizes the supported chromium oxide as $\text{Cr}(\text{VI})$ in tetrahedral coordination and the relative ratio of dimers/ monomers increases with increasing chromium oxide coverage on the alumina support. The surface chromium oxide species are stable at elevated calcinations temperatures and upon dehydration [10].

Ziyad *et al.* [11] studied the effect of phosphorus additive on $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalyst for ODH of ethane and observed that the chromium oxide notably increases the activity of toward the total oxidation of hydrocarbon. Furthermore, the addition of phosphorus to the system, simultaneously improved the global conversion and the ethylene selectivity. Characterization of catalysts was achieved by XRD, EPR and UV-visible spectroscopy. XRD revealed that the TiO_2 did not suffer any structural modification after impregnation. EPR and UV-visible spectroscopies revealed that the sample essentially contained Cr^{6+} and Cr^{5+} ions, which were not very efficient in mild

oxidation. A fairly good correlation was established between the catalysts acidity, the P/Cr ratios, and the activity in the ODH reaction. It was found that an excess amount of phosphorus increased the acidity, but decreased the conversion. An optimum P/Cr ratios equal to 1.6 was determined. The improvements in catalytic activity were attributed to the appearance in the samples of phosphates and clustered Cr³⁺ ion. The phosphorus probably also contributed to the stabilizing the octahedral Cr³⁺ species in a well defined environment and adjusted in an advantageous way the acid properties of the active surface.

Kordulis *et al.* [12] studied the effect of composition on the physico-chemical properties and catalytic performance for the SCR of NO with NH₃ over chromia- vanadia catalysts supported on TiO₂. Catalysts were prepared in such a way that the total moles of Cr+V were constant by taking different mole% of Cr and V. They found that best catalytic performance was achieved by the catalysts containing 2 mol% Cr and 6 mol% V (TiCr₂V₆), while all the binary active phase-containing catalysts proved to be more active than the corresponding single active phase- containing catalysts, at reaction temperature higher than 350°C. The enhanced catalytic performance of the binary active phase- containing catalysts is attributed to a synergy developed between the two active phases. This synergy is maximized in the TiCr₂V₆ sample, where a new Raman band at 971 cm⁻¹ was attributed to isolated Cr⁶⁺ species decorated by well dispersed V⁵⁺ species. They found that the existence of chromia phase on the titania support stabilizes the texture of the final TiCr_xV_y catalysts against change provoked by deposition of the vanadia phase.

Wong and Nobe [19] studied the catalytic performance of the following catalysts for SCR reaction: Cr₂O₃/TiO₂, V₂O₅/TiO₂ and V₂O₅-Cr₂O₃/TiO₂. In all these

catalysts the total active phase loading was 10 wt% and the ratio of vanadium to chromium oxide was 20:1. Their results showed that V_2O_5/TiO_2 catalysts were more active and selective than Cr_2O_3/TiO_2 catalysts, while the activity and selectivity of $V_2O_5-Cr_2O_3/TiO_2$ catalysts were comparable to those of V_2O_5/TiO_2 catalysts.

Chromium oxide catalysts unsupported or supported mainly on TiO_2 (anatase) have been extensively studied over the last decade for the SCR of NO with NH_3 in the presence of excess oxygen by the groups of Baiker and of Curry-Hyde [13-16]. They have proved that chromium oxide based catalysts containing amorphous chromia as the active phase are quite promising catalysts for low temperature SCR operations.

Huff and Flick [5] examined unpromoted Cr_2O_3 and Pt modified Cr_2O_3 coated ceramic foam monoliths and Cr_2O_3/Al_2O_3 pellet catalysts. These catalysts were chemically characterized using ODH of ethane at very short contact time. C_2H_4 selectivity and C_2H_6 conversion was reduced with the addition of Pt.

Vurman et al. [17] studied the structural influence of the additives on supported vanadia catalysts using IR and Raman spectroscopy and observed that additives like W,Mo etc. increase the concentration of the polymerized species. Similar behaviour was observed when chromia supported on alumina, titania and niobia catalysts are modified with tungsten and molybdenum [18]

Cherian et al. [20] reports that the effect of dopants on supported chromium oxide catalysts alter the state of surface metal oxide species by introducing changes in electronic properties, acid-base properties, structural arrangements, size of the atoms clusters and the adsorption properties. For example if an alkaline earth metals are added, the lewis acidity is decreased, non-metallic dopant (SO_4^{2-} , PO_4^{4-}) will increase the lewis acidity, elements such as Mo^{4+} , W^{4+} , V^{4+} etc. which are noninteractive will

not affect the structural of surface chromyl species, however, will be competitive with the basic sites of the support in the reaction. The effect of additives on the reactivity of each supported catalysts will be unique as their influence on the activity depends upon the reaction mechanism.

Trunschke et al. [21] has studied the influence of lanthanum on the nature of surface chromium species in La_2O_3 - modified $\text{CrO}_x/\text{ZrO}_2$ catalysts. The TPR studies didn't reveal any difference in the modified and unmodified $\text{CrO}_x/\text{ZrO}_2$ catalysts. However, La_2O_3 addition stabilizes $\text{CrO}_x/\text{ZrO}_2$ catalyst sintering. Furthermore, anchoring of chromium oxide species, isolated Cr^{3+} and highly dispersed Cr_2O_3 species are facilitated due to the increased number of nonacid hydroxyl groups.

Sloczynski et al. [29] performed ODH of isobutane on chromia supported on SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , and MgO . They also examined the potassium-modified catalysts. The supported catalysts have found to be active in the ODH of isobutene at relatively low temperatures 200-400°C, the total activity and selectivity to isobutene depending on the nature of the support and the potassium presence. The highest selectivity to isobutene (70% at 5% conversion) and the isobutene yields of 9% have been obtained for CrOx/TiO_2 and K- promoted $\text{CrO}_x/\text{Al}_2\text{O}_3$ preparations.

Literature on ODH of Propane

Lemonidou et al. [21] conducted the ODH of propane using vanadia type catalysts supported on Al_2O_3 , TiO_2 , ZrO_2 and MgO . They also attempted the promoted catalysts with alkali metals (Li, Na, K). It was observed that $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst exhibits the highest activity in ODH of propane. It was also identified that V_2O_5 supported on Al_2O_3 catalysts exhibits the highest selectivity. The addition of alkali metals

decreased the catalytic activity in the order nondoped>Li>Na>K, however, propane selectivity significantly increased in the presence of doped catalysts.

Kung [8] summarized the ODH of light alkanes (C₁-C₄). It was observed that there is a limitation in obtaining higher yields of alkene since dehydrogenation of alkanes is a consecutive reaction. The degradation of alkenes being favored compared to the ODH of light alkanes. They also reported that a very high selectivity for alkene at high conversion can be obtained in the presence of a suitable catalysts and absence of gaseous oxygen. V-Mg-O was found as the most selective for alkene yield. The selectivity of propene for ortho and pyrovanadate were similar, but metavanadate showed poor selectivity.

Ermini et al. [22] conducted the ODH of propane reaction over alumina supported V-Mn-K oxide catalysts. The addition of K to V₂O₅/Al₂O₃ catalyst decreased the activity but significantly increased the propene selectivity. This was found to be due to the poisoning of the acidic sites of alumina supports that is responsible for the degradation of propene. Conversely the addition of Mn decreased both the activity and selectivity. In both cases the co-ordination state of vanadia sites was perturbed with an increase of the crystal field.

Watling et al. [23] performed ODH of propane over niobia supported vanadium oxide catalysts, which is another type of supported metal oxide catalysts. All the sample showed similar TOF. It was noted that the key factor for the design of an active and selective catalysts for the ODH of propane conversion is the optimization of propane adsorption.

Ozkan et al. [24] investigated the ODH of propane over silica-titania mixed oxide supported molybdenum catalysts. The effect of alkali (potassium)

doping on the catalysts was studied. It was observed that by varying the K/Mo molar ratio a maximum in selectivity and yield of propene was obtained. The maximum yield of propene obtained in dilute feed experiments was ~ 30%.

Zehrani et al. [25] conducted the ODH reaction over alumina-supported oxides of V, Cr, Mn Zr and Ba. They found that the maximum propane conversion (26%) and selectivity to olefine (70%) were achieved with vanadium oxide at 450°C. The other metal oxides showed lower conversion (9-17%) and olefins selectivity (36-58%). They explained these results on the basis of the lattice oxygen reactivity as estimated from the reduction potential of the metal cations. Metals whose cation has high potential (e.g. vanadium oxide containing catalysts) were found to favor low CO_x and high selectivity to propene and ethene.

Creasor and Anderson [26] made kinetic investigation in to the ODH of propane over V-Mg-O catalysts. Propane was found to react with surface oxygen species to form adsorbed propylene capable of subsequent desorption from the solid surface.

Baldi and coworkers [27] investigated the mechanism of ODH of propane over manganese oxide using FT-IR spectroscopy. At reaction temperature range of 573 to 753 K, and for propane to oxygen ratio of 1:1, high selectivity and significant productivities are obtained. Flow reactor and FT-IR data strongly support the proposal that main by- reaction under these conditions is the propane combustion through propene formation and over-oxidation to CO₂. With higher concentration, a parallel combustion route becomes relevant, with further decrease in propene selectivity. The π -bonded surface complexes formed by the direct interaction of propene with the catalyst cationic centers are main precursors for the propane over-oxidation, while adsorbed isopropoxides are likely intermediates in the ODH of propane.

Very recently Cherian et al. [28] reported the structure-reactivity relationship for ODH reaction over supported chromium oxide catalysts. The surface species were found to be more active than the bulk Cr_2O_3 for the partial oxidation of propane to propene. The selectivity to propene for the catalysts increased with loading, however, the TOF of both sets of catalysts decreases with increase in loading.

1.7 Objectives

It appears from the above literature that the various additives can influence the behavior of supported metal oxide catalysts in general and supported chromium oxide catalysts in particular. These additives include like potassium, lithium oxides, tungeston, niobium, lanthanum oxides, and oxides of rare earth elements etc. Little work, however, has been done on the modifying chromium oxide catalysts. Furthermore, research on using modified chromium oxide catalysts for the ODH of propane is even more sparse. Thus a more detailed study of modified supported chromia catalysts is required since these catalysts have shown the promise towards the ODH of propane.

The present study addresses the effect of additives on the reactivity of the surface chromia species towards the ODH of propane. Two additives, vanadium and sodium are chosen. Various amounts of additives (Na, V) are doped to chromia catalysts supported over Al_2O_3 and TiO_2 . These promoted catalysts are initially characterized and then studied for the ODH of propane at different temperature to understand the structure-reactivity relation of the modified supported chromium oxide catalysts.

Thesis outline

Chapter two deals with experimental details used to synthesize and characterize the modified chromia catalysts. Results of the experiments, described in Chapter 2, are presented in Chapter 3. Chapter 4 discusses the results obtained and finally in Chapter 5, the conclusions obtained in the present study are stated.

In each Chapter, the figure and tables are arranged at the end in numerical order. At the end of the thesis, the references are given and numbered as they appear in the text.

Chapter 2

Experimental Procedure

2.1 Preparation of Catalysts Samples

2.1.1 Pretreatment of Support

Pure Titania (Degussa, 56 m²/gm) and γ Alumina (Condea, 180 m²/gm) were used as the supports for the preparation of supported chromium oxide catalysts. The supports are pretreated by forming a paste with incipient amount of double distilled water, and then dried at room temperature for 12 h, followed by heating at 383 K for 12 h. The samples were finally calcined at 723 K for TiO₂ and 773 K for Al₂O₃. The final calcination temperature was achieved by step increment of 323 K and kept at the new temperature for 0.5 h.

2.1.2 Preparation of supported chromium oxide catalysts

The precursor used for preparing the supported chromia catalysts was chromium nitrate [Cr(NO₃)₃.9H₂O, Aldrich, 99.99% purity]. A solution was prepared by adding double distilled water to calculated amount of precursor corresponding to a given Cr₂O₃ loading. The pretreated support (TiO₂ or Al₂O₃) was intimately mixed with incipient volumes of the solution prepared in order to form a paste. The paste formed by the precursor and support was dried at room temperature for 12 h, followed by heating at 383 K in an oven and finally calcined at 723 K for TiO₂ based samples and 773 K for Al₂O₃ based samples. A 1% Cr₂O₃/TiO₂ and 5% Cr₂O₃/Al₂O₃ sample were chosen, which corresponded to \sim 0.3 and \sim 0.4 surface coverage, respectively.

2.1.3 Preparation of modified catalyst samples

Catalysts modified by sodium and vanadium were prepared by using solution of sodium hydroxide (NaOH, 20% solution) and ammonium-metavanadate (CDH, 98% solution), respectively, to previously prepared 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ or 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples. Solutions with double distilled of water were made with amounts of NaOH corresponding to Na/Cr weight ratios of 0.02, 0.06, 0.1 and 0.15. For making vanadium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ammonium-metavanadate was dissolved in a solution of oxalic acid to form V/Cr weight ratios of 0.5, 1.0, 1.5. Vanadium modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ were made by in reverse sequence. Initially, known amounts of vanadium were deposited on the TiO_2 surface using ammonium- metavanadate/ oxalic acid solution such that the V/Cr weight ratios are 0.5, 1.0, and 1.5. Then solution of ammonium dichromate ($(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, Nice , 99.5% purity) was dissolved in double distilled water and mixed to the previously prepared catalysts. The amount of chromium oxide precursor was added in amounts corresponding to the formation of 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$. The heat treatment procedure was similar to the preparation of unmodified catalysts given above.

These modified catalysts were denoted as AlCr_yV_x and AlCr_yNa_x , Where x and y represents the weight ratio of V/Cr and Na/Cr, respectively. The same nomenclature was used for modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ samples also, i.e., TiCr_yV_x and TiCr_yNa_x .

2.2 Characterization Techniques

Characterization of any catalyst involves physical and chemical characterization. Physical characterization was achieved by using Raman spectroscopy, BET, XRD, TPR and EPR

studies. Catalysts were chemically characterized by TPR and for their reactivity in the oxidative dehydrogenation of propane.

2.2.1 Physical Characterization

2.2.1.1 Surface Area Measurement

Surface area is the important factor in catalysis since it determines the dispersion and the activity of the catalysts, and, consequently the activity of the catalysts. The total BET surface area of the catalysts sample were carried out on a COULTER SA3100 instrument equipped with a version 2.12 SA-view software. Samples were pretreated by evacuating the adsorbed gases at high temperature (393 K) from the sample.

Nitrogen adsorption method was used for analyzing the BET surface area. Nitrogen gas was added in known quantity in to an evacuated tube containing the sample. By keeping the temperature constant the quantity of the gas adsorbed and pressure of the sample was monitored continuously. The BET plot was constructed from the isotherm formed, and the BET constants were calculated. The slope and intercept from the BET plot gave the monolayer volume of the adsorbate. Surface area was calculated form the following formula :

$$S=4.35*10^4*V_m \text{ cm}^2/\text{gm of catalyst}$$

Where V_m is monolayer volume of adsorbed nitrogen.

2.2.1.2 X-Ray Diffraction (XRD)

X-ray diffractograms reveal the specific phases present in samples. It also reveals the crystalline nature of the catalysts. XRD pattern were obtained with a Reich Seifert ISO-Debeyflex 2002 instrument powered by a nickel filtered CuK_α radiation ($\lambda= 1.5406000 \text{ \AA}$) with a generator setting at 40 KV and 30 mA. The diffractometer was operated

with a 20° diverting and receiving slit at a scan rate of 3° / min (in 2θ degrees) with a chart speed of 30 mm/min. All samples were crushed to 200-mesh particle size and packed in the well of a horizontally positioned sample holder. The quantitative analysis of the diffraction patterns was done by comparing the calculated values of intensity and crystallites dimension with relevant ASTM powder diffraction file data for identification of the catalysts phase present.

2.2.1.3 Raman Spectroscopy

The laser Raman spectra of the vanadia modified 5% Cr₂O₃/Al₂O₃ catalysts alongwith unmodified 5% Cr₂O₃/Al₂O₃ catalyst under ambient conditions were obtained by means of an argon ion laser (spectra Physics, Model 165). The 514.5 nm line was used as the exciting source. The laser power delivered at the sample was 15-40 mW. The scattered radiation from the sample was collected and directed into a triplemate spectrometer (Spex, model 1877) coupled to a optical multichannel analyzer (Princeton applied research, model 1463) with an intensified photodiode array detector thermoelectrically cooled to -35 °C. About 200 mg of the catalysts was pressed in to self-supporting wafers and placed in a rotating sample cell, to avoid local heating effects.

2.2.1.4 Electron Paramagnetic resonance studies

EPR studies were performed on a Varian – E- 109 X band spectrometer. The spectra were obtained at room temperature using a microwave frequency ~9.15 GHz and a microwave power 10mW. The scan time was 8 min and magnetic field modulation frequency was 100 kHz. The EPR spectra were calibrated with DPPH using a duel cell.

2.2.2 Chemical characterization

The catalyst samples were chemically characterized by temperature programmed reduction and the ODH of propane reaction.

2.2.2.1 Temperature programmed reduction (TPR) studies

TPR experiment were carried out using a mixture of 10% H₂/Ar at 1 bar pressure. Helium was used as carrier gas and also for degassing the sample. The sample weight was 50 mg. The samples were precalcined *in situ* at 523 K in helium environment for 15 minutes in order to remove the moisture and adsorbed gases present in the sample. The samples were then cooled to 50 °C. A H₂/Ar mixture was then passed over the sample at a flow rate of 50ml/min. TPR measurements were carried out by increasing the temperature at a rate of 10 K/min up to 973 K. The hydrogen gas in the exit gas stream was monitored using a TCD.

2.2.2.2 Reaction studies

Steady-state reaction experiments were carried out in a vertical down-flow quartz reactor at atmospheric pressure. The experimental set up is shown in Fig.2.1. The quartz reactor was made by connecting a 15 cm long and 10 mm i.d. tube with another 15 cm long and 5 mm i.d. tube. These two sections were connected by a tapered region. A mixture of catalyst sample and quartz glass pieces to form a bed height of 1cm was placed just above the tapered region on quartz wool. The purpose of the quartz pieces was for dilution of the catalysts bed to avoid mass and heat transfer effects. The weight of the catalysts was 100 mg for all the reaction studies. The reactor tube was mounted vertically in a tubular furnace. The temperature of the reactor and catalyst bed was measured by a

Chromel-Alumel thermocouple inserted inside the reactor tube just above the catalysts bed and was controlled by a PID temperature controller (FUJI Micro- controller X Model PXZ 4). The propane flow rate was controlled by a thermal mass flow controller (Bronkhost Hi-tech, Model F-201 D FAC-22-V) and air was adjusted through a rotameter (Eureka, Model SRS/MG-5). The propane and air ratio was maintained at 3:1.

The products gases were analyzed using an online NUCON 5765 gas chromatograph at an oven temperature 329 K. A methanizer was used to convert carbon oxides (CO and CO₂) to methane. The carbon oxides and hydrocarbons were separated using activated-alumina column by a flame ionization detector (FID). Runs were taken at different temperatures starting from 623 to 723 K with a constant total flow rate of 40 cc/min. The experiments were performed such that the conversion was limited to 5%. Consequently, differential analysis of the reaction data is valid.

Calculation

The products analyzed from the outlet of the reactor were propene, carbon oxides, and unreacted propane. The peak area corresponds to a particular amount (mole) of specific gas in the injected sample, which was determined by multiplying the peak area with sensitivity factors given by Dietz [32]. The true area represents the weight of each component. Conversion, selectivity and yield were calculated using the formulae given below:

$$\text{Conversion}(X), \% = \frac{npi - npo}{npi} \times 100$$

$$\text{Selectivity}(S_i), \% = \frac{ni}{npi - npo} \times 100$$

$$Yield(yi), \% = \text{Conversion} \times \text{selectivity} = \frac{ni}{npi} \times 100$$

Where

npi = no. of moles of propane at the inlet

npo = no. of moles of propanes at the outlet

ni = no. of moles of product (propene) in the exit stream

Activation energy

The activation energy is the excess energy over that of the ground state, which an atomic system must acquire to permit a particular process to occur. The activation energy (E) for propene formation was calculated by the following equation

$$\ln(yield) = \ln(A) - \frac{E}{RT}$$

The slope of the line between $\ln(yield)$ and $1/T$ gives E/R value, where R is the universal gas constant and A is the frequency factor. Overall activation energy is calculated on the basis of conversion value. The slope of the line between $\ln(\text{conversion})$ and $1/T$ gives the overall activation energy.

Table 2.1 Experimental parameters for reaction studies

PARAMETER	VALUE
Reactor	Quartz tube Reactor, 10 mm ID
Air flow rate (ml/min)	25
Propane flow rate (ml/min)	15
Total gas flow rate (ml/min)	40
Reactor Temperature range (°C)	350-450
Amount of catalyst (mg)	100
Column temperature of GC (°C)	55

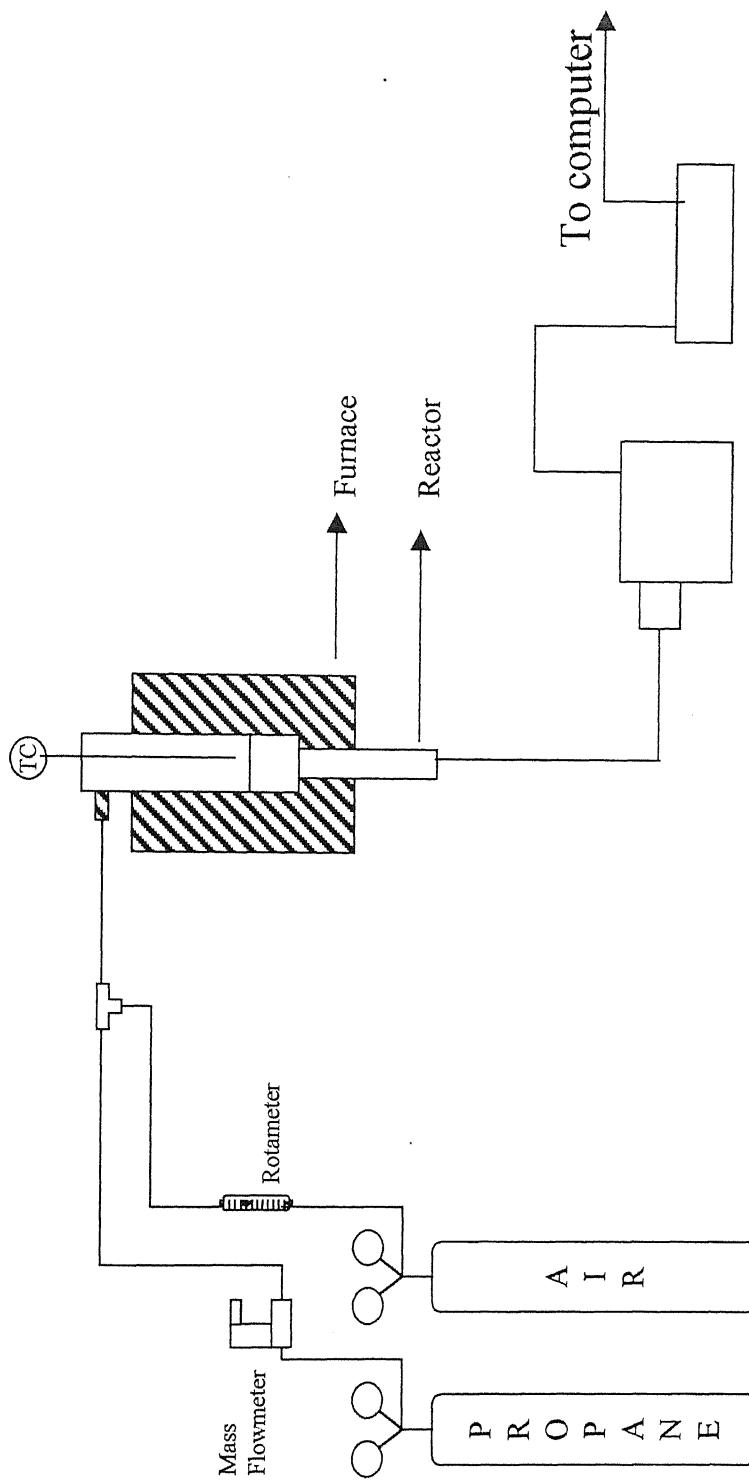


Figure 2.1 Schematic diagram of reactor setup

(Feed Control Section)

(Reaction Section)

(Analysis Section)

Gas Chromatograph Data Station

Chapter 3

Results

A series of modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ and 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ along with the unmodified samples were prepared according to given M/Cr ratios where M is the additives species. These samples were characterized by various techniques. Physical characterization of the sample was achieved by studying the colour, surface area, XRD pattern and by Raman and EPR spectroscopy. The catalysts were chemically characterized using TPR with hydrogen and ODH of propane reaction.

3.1 Colour

The unmodified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts was light yellow in colour. As the amount of sodium was increased the sample becomes more intense yellow in colour. The colour of vanadium modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts gradually changed from light yellow to gray with an increase in vanadium oxide loading. The colour of 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ was yellow and it changed from yellow to brown for vanadia-modified sample. The colour of sodium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample remained the same (yellow) as sodium was added.

3.2 Surface Area

The surface area of modified and unmodified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ were determined and are given in Tables 3.1, 3.2 and 3.3 along with the M/Cr ratio, atomic ratio, Wt. % of Cr_2O_3 and Wt. % of V_2O_5 or Na_2O . For reference, the surface area of Al_2O_3 and TiO_2 are $201 \text{ m}^2/\text{g}$ and $60 \text{ m}^2/\text{g}$ respectively [18]. The surface area for vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts given in Table 3.1 decreases with

increase in vanadium oxide loading. The chromium oxide amount was same in all of these catalyst samples. The surface area for vanadium oxide modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ given in Table 3.2, however, remained relatively constant. The surface area for sodium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$, given in Table 3.3, are also relatively constant.

3.3 XRD Studies

XRD patterns of vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ were obtained and shown in Fig 3.1 along with the alumina support and 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample. The XRD patterns of vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and unmodified sample were similar to the Al_2O_3 support with peaks at 48° and 68° . No new peaks were detected. Similarly the vanadium oxide modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ and Sodium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ samples do not reveal any peaks besides those due to the oxide support.

3.4 Raman Spectra

The Raman spectra of vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ are shown in the Fig. 3.2 along with the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ spectra as reference. These spectra were obtained under ambient conditions. Two bands at 900 cm^{-1} and 367 cm^{-1} along with a weak band at 213 cm^{-1} are observed for 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample. These peaks are assigned to surface chromium oxide species [17]. Addition of 3.1% vanadium oxide to 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample does not affect the positions of the bands due to the surface chromium oxide species. Addition of 6.0% and 8.8% vanadium oxide to 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample, however, shows a distinct Raman band at $\sim 811\text{ cm}^{-1}$ and shoulder at $\sim 950\text{ cm}^{-1}$ in addition to the bands due to the surface chromium oxide species.

3.5 EPR Spectra

The EPR spectra showing the effect of modifying the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ with vanadium and sodium are shown in Fig 3.3 to Fig 3.6. The presence of a strong axially symmetric peak centered around 3400G ($g=1.96$, $\Delta H= 40-60$ G) in unmodified and vanadium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts as shown in Fig 3.3. The intensity of the peak, corresponding to Cr^{5+} γ -signal, decreases as vanadia content increases. At high vanadium oxide loadings, the EPR spectra also contain Cr^{3+} species (β signal) that are not clearly identified due to the presence of strong Cr^{5+} signal.

The EPR spectra of sodium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples are shown in Fig 3.5. The spectrum of 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ is included as reference. Addition of sodium to the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ does not change the spectra since the symmetric peak due to Cr^{5+} is unaffected and its intensity remains relatively constant.

The EPR spectra of vanadium and sodium modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ are shown in Fig.3.4 and 3.6. The spectrum of unmodified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ is included as reference. Unmodified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ exhibited the typical sharp Cr^{5+} γ signal ($g=1.96$ and $\Delta H= 30-40$ G). For the presence of vanadium oxide in the 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ no additional peaks were observed, however, the intensity of Cr^{5+} species decreased as the vanadium oxide amount increased. Sodium modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts also revealed only Cr^{5+} γ signal ($g=1.96$ and $\Delta H= 45$ G), but the intensity of the Cr^{5+} species was lower than unmodified sample.

3.6 TPR Studies

TPR studies were performed on modified and unmodified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ and 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples. The pure supports (Al_2O_3 and TiO_2) did not reveal any reduction in the temperature range considered.

The TPR profiles for vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ are plotted in Fig 3.7. Fig. 3.7 reveals that the TPR profile of unmodified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample (AlCrV_0) shows a single peak, T_{\max} , at 389°C . Modifying the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ with increasing amounts of vanadium oxide, as in $\text{AlCrV}_{0.5}$ and $\text{AlCrV}_{1.0}$, two peaks are observed at ~ 387 and $\sim 490^{\circ}\text{C}$. The normalized (per gram) intensity of the TPR peak at $387\text{--}389^{\circ}\text{C}$ is constant for AlCrV_0 and $\text{AlCrV}_{0.5}$ samples but decreases in intensity for the $\text{AlCrV}_{1.5}$ sample. Furthermore, the intensity of the peak at 490°C increases with addition of vanadium oxide and is of similar intensity to the $387\text{--}389^{\circ}\text{C}$ peaks for the $\text{AlCrV}_{1.5}$ sample.

The TPR profiles for vanadium oxide modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ samples are shown are in Fig. 3.8 along with the unmodified sample. Fig. 3.8 reveals that the TPR profile of the unmodified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ sample (TiCrV_0) shows a single peak, T_{\max} , at 368°C . Modifying the 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ with vanadium oxide, as in $\text{TiCrV}_{0.5}$ and $\text{TiCrV}_{1.5}$, two peaks are observed at 368 and 448 to 460°C . The intensity of the peak at $\sim 368^{\circ}\text{C}$ remains relatively constant for the TiCrV samples. The intensity of the peak at $448\text{--}460^{\circ}\text{C}$, however, increases with an increase in vanadium oxide.

TPR studies were also carried out over sodium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ ($\text{AlCrNa}_{0.06}$ and $\text{TiCrNa}_{0.06}$). From the TPR plot a single T_{\max} is observed. From the peak area and calibration amounts of hydrogen the amount of

hydrogen consumed per gram of the sample is determined and converted to H/Cr ratios. In Table 3.4 the T_{max} temperature and H/Cr ratios are given for the sodium modified and unmodified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ samples. From the table it is observed that the addition of sodium slightly increases the T_{max} temperature and noticeably decreases in H/Cr ratio.

3.7 ODH Of Propane

The ODH of propane for modified and unmodified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ and 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ were performed at temperatures ranging from 350–450 $^{\circ}\text{C}$. The results of these studies are given below.

3.7.1 Effect of vanadium modified catalysts

For vanadium modified and unmodified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts sample, the variation of conversion with temperature is given in Fig 3.10. Fig 3.10 reveals that all the curves are nonintersecting and the conversion increases monotonically with temperature for all of these catalysts. For vanadium oxide modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ sample the conversion was higher than the unmodified sample and increases with increasing vanadium content at all temperatures. For example, at 400 $^{\circ}\text{C}$ the conversion of TiCrV_0 , $\text{TiCrV}_{0.5}$, TiCrV_1 and $\text{TiCrV}_{1.5}$ are 0.7%, 1.1%, 1.4%, and 1.8% respectively.

Fig 3.12 shows the variation in the propene selectivity with temperature for the same series of vanadium oxide modified samples. The initial addition of vanadium oxide modified to the 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalyst increased the propene selectivity at all temperatures. The propene selectivity for the $\text{TiCrV}_{0.5}$ and $\text{TiCrV}_{1.0}$ samples remained higher than the unmodified catalysts at all temperatures, however, the selectivity decreased for the $\text{TiCrV}_{1.5}$ sample to values similar to the unmodified catalyst at 460 $^{\circ}\text{C}$.

In this series of vanadium modified samples the highest selectivity was achieved by the TiCrV_1 sample.

The conversion of propane as a function of reaction temperature for vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts along with the unmodified sample (AlCrV_0) is shown in Fig 3.9. From fig. 3.9 it is observed that conversion increases with temperature for the vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts. Unlike the TiCrV series of catalysts the conversion versus temperature curves were intersecting at lower temperature ($<400^\circ\text{C}$). At 420°C and higher temperature the increase in conversion with addition of vanadium oxide was evident. For example, at 420°C the conversion of AlCrV_0 , $\text{AlCrV}_{0.5}$, AlCrV_1 , and $\text{AlCrV}_{1.5}$ are 2.0, 2.4, 2.7 and 2.8% respectively.

Fig 3.11 shows the variation in selectivity of vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst with temperature. It is clear from Fig. 3.11 that the selectivity increases with temperature for this series of catalysts. For example, the selectivity to propene for the AlCrV_0 sample increases from 68.8 to 70.68 to 75.5 to 84.3% when the temperature increases from 380 to 400 to 420 to 450°C . Selectivity also increases with increasing vanadium oxide content in the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample at each temperature. For example, at 400°C the selectivity of the AlCrV_0 , $\text{AlCrV}_{0.5}$, AlCrV_1 and $\text{AlCrV}_{1.5}$ are 70.7, 77.6, 85.7, and 89.2%, respectively.

3.7.2 Effect of sodium modified catalyst

The effect of sodium addition to the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst for the ODH of propane was also investigated in the $380-450^\circ\text{C}$ temperature range. Conversion as a function of temperature for sodium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ is shown in Fig 3.13 in the form of bar charts. As mention above the conversion of 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ increases with temperature.

Similar trends are also observed with the sodium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts. At each temperature, however, the propane conversion decreased with the incremental addition of sodium to the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample, except at 380 and 400 $^{\circ}\text{C}$. At 380 and 400 $^{\circ}\text{C}$ the conversion for $\text{AlCrNa}_{0.06}$ was greater than $\text{AlCrNa}_{0.15}$ (general trend) but smaller than $\text{AlCrNa}_{0.02}$ (anomalous behavior). A similar decrease in propane conversion was observed with the addition of sodium to the 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ as shown in Fig. 3.15. This decrease in propane conversion was evident at all temperatures considered.

The effect of sodium addition to the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ samples on the propene selectivity are shown in Figs 3.14 and 3.16, respectively. From the figures it is observed that the propene selectivity increases with temperature for the sodium modified catalysts. However, at each temperature the formation of CO_x increased with addition of sodium. Consequently, at each temperature the propene selectivity decreased with the addition of sodium to the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts.

Table 3.1 Composition and specific surface area of 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts modified with various amount of vanadium

Catalysts	Wt. Ratio (V/Cr)	Atomic ratio (V/Cr)	Cr_2O_3 Weight %	V_2O_5 Weight %	Surface Area (m^2/gm)
AlCrV_0^*	0	0	5	0	183
$\text{AlCrV}_{0.5}$	0.5	0.5	5	3.1	171
AlCrV_1	1.0	1.0	5	6.0	166
$\text{AlCrV}_{1.5}$	1.5	1.53	5	8.8	163

* In AlCr_yV_x , x/y represents the weight ratios of V/Cr

Table 3.2 Composition and specific surface area of 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts modified with various amount of vanadium

Catalysts	Wt. Ratio (V/Cr)	Atomic ratio (V/Cr)	Cr_2O_3 Weight %	V_2O_5 Weight %	Surface Area (m^2/gm)
TiCrV_0^*	0	0	1	0	38
$\text{TiCrV}_{0.5}$	0.5	0.5	1	0.6	41
TiCrV_1	1.0	1.0	1	1.2	42
$\text{TiCrV}_{1.5}$	1.5	1.5	1	1.8	40

* In TiCr_yV_x , x/y represents the weight ratios of V/Cr

Table 3.3 Composition and specific surface area of 5% Cr₂O₃/Al₂O₃ and 1% Cr₂O₃/ TiO₂ catalysts modified with various amount of sodium

Catalysts	Wt. Ratio (Na/Cr)	Atomic Ratio (Na/Cr)	Cr ₂ O ₃ Weight %	Na ₂ O Weight %	Surface Area (m ² /gm)
AlCrNa ₀	0	0	5	0	183
AlCrNa _{0.02}	0.02	0.045	5	0.09	179
AlCrNa _{0.06}	0.06	0.136	5	0.29	179
AlCrNa _{0.1}	0.10	0.226	5	0.48	180
AlCrNa _{0.15}	0.15	0.339	5	0.7	180
TiCrNa _{0.06}	0.06	0.136	1	0.06	43

Table 3.4 TPR data for sodium doped 5% Cr₂O₃/Al₂O₃ and 1% Cr₂O₃/TiO₂ catalysts

Catalysts	T _{max}	H/Cr
AlCrNa ₀	390	1.68
AlCrNa _{0.06}	395	1.19
TiCrNa ₀	364	1.76
TiCrNa _{0.06}	372	1.56

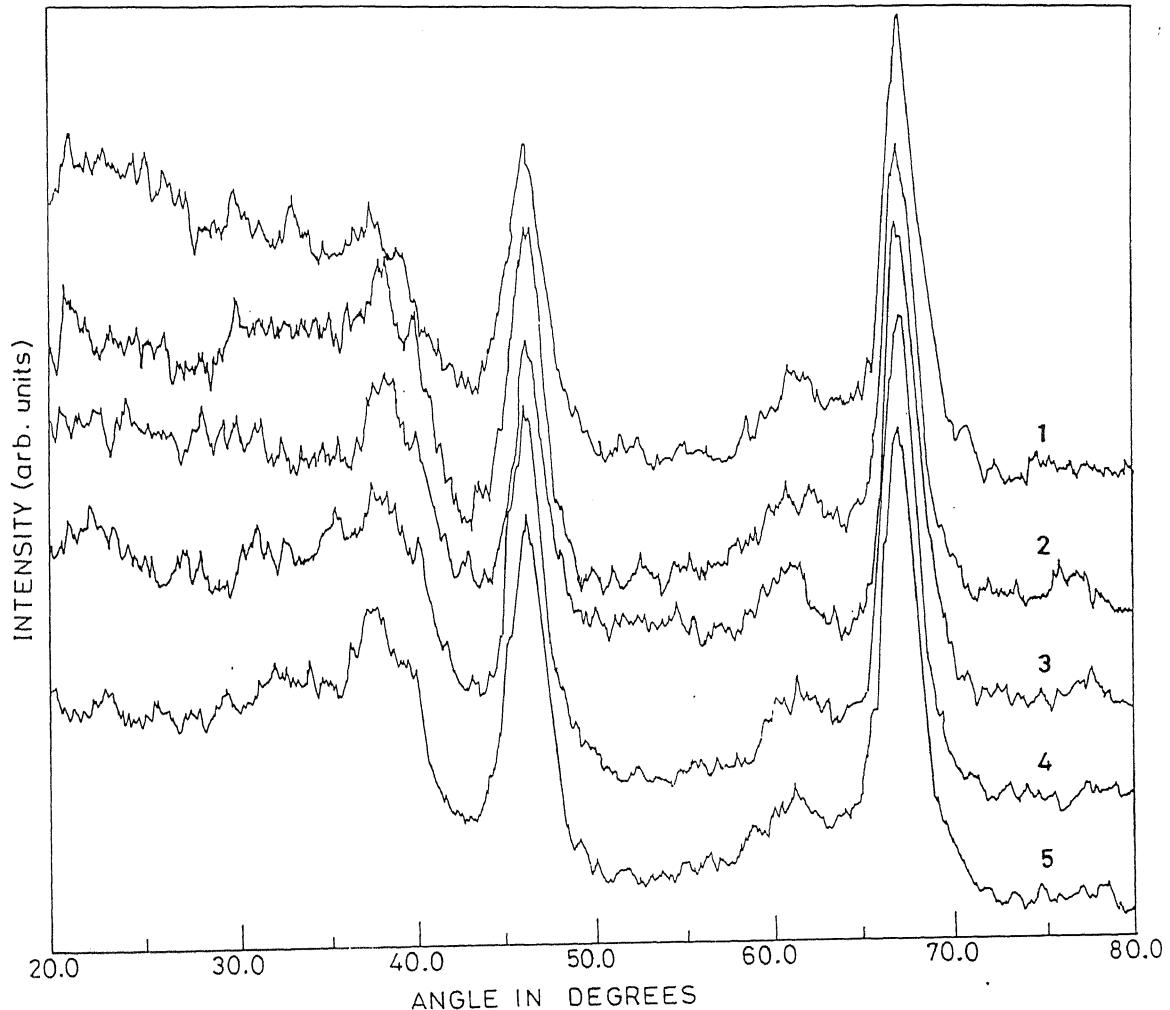


Figure 3.1 XRD plot of the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ modified with vanadium oxide
1) $\text{AlCrV}_{1.5}$ 2) $\text{AlCrV}_{1.0}$ 3) $\text{AlCrV}_{0.5}$ 4) AlCrV_0
5) Pure Al_2O_3 support

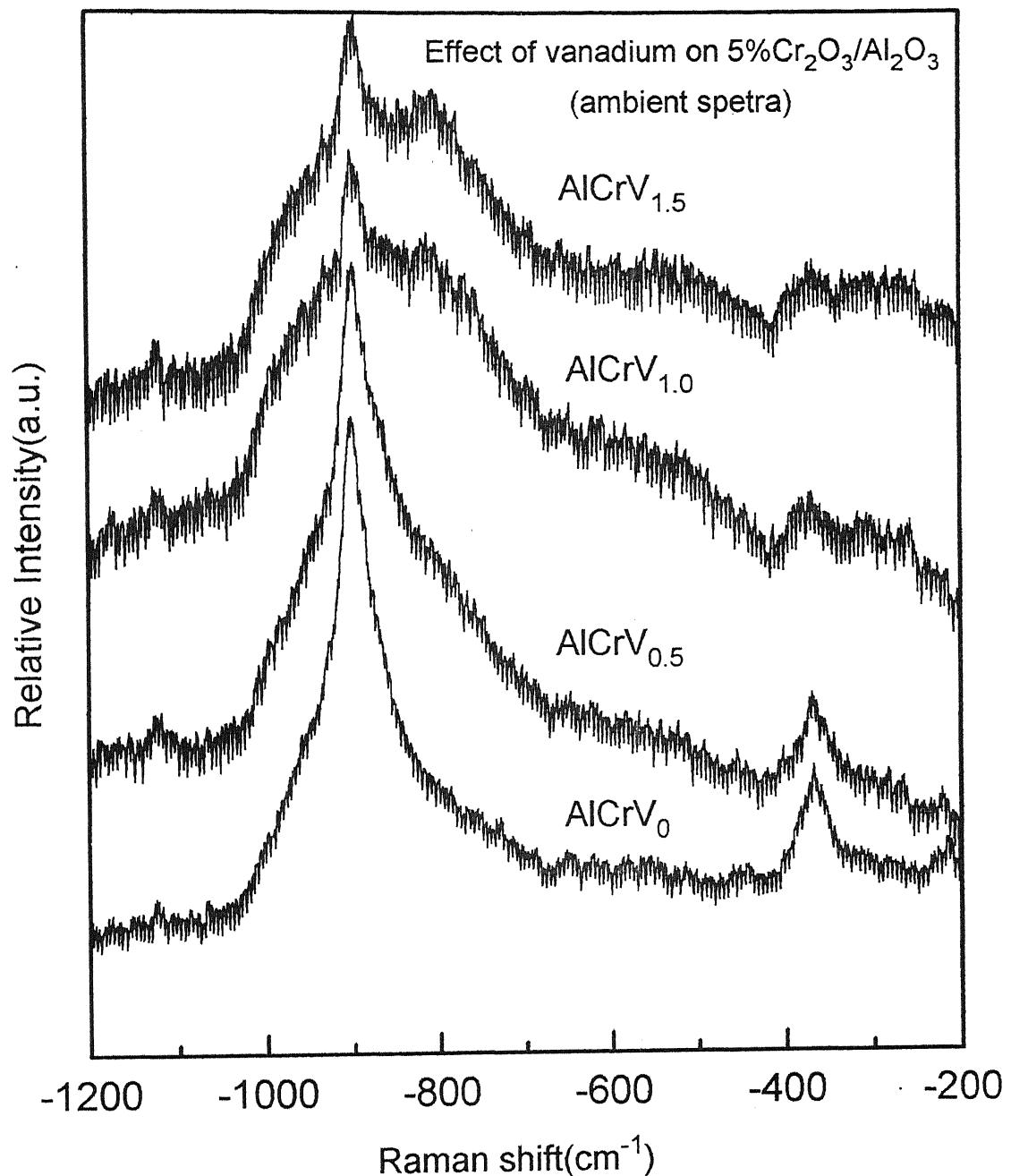


Figure 3.2 Ambient Raman Spectra of the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ modified with vanadium oxide

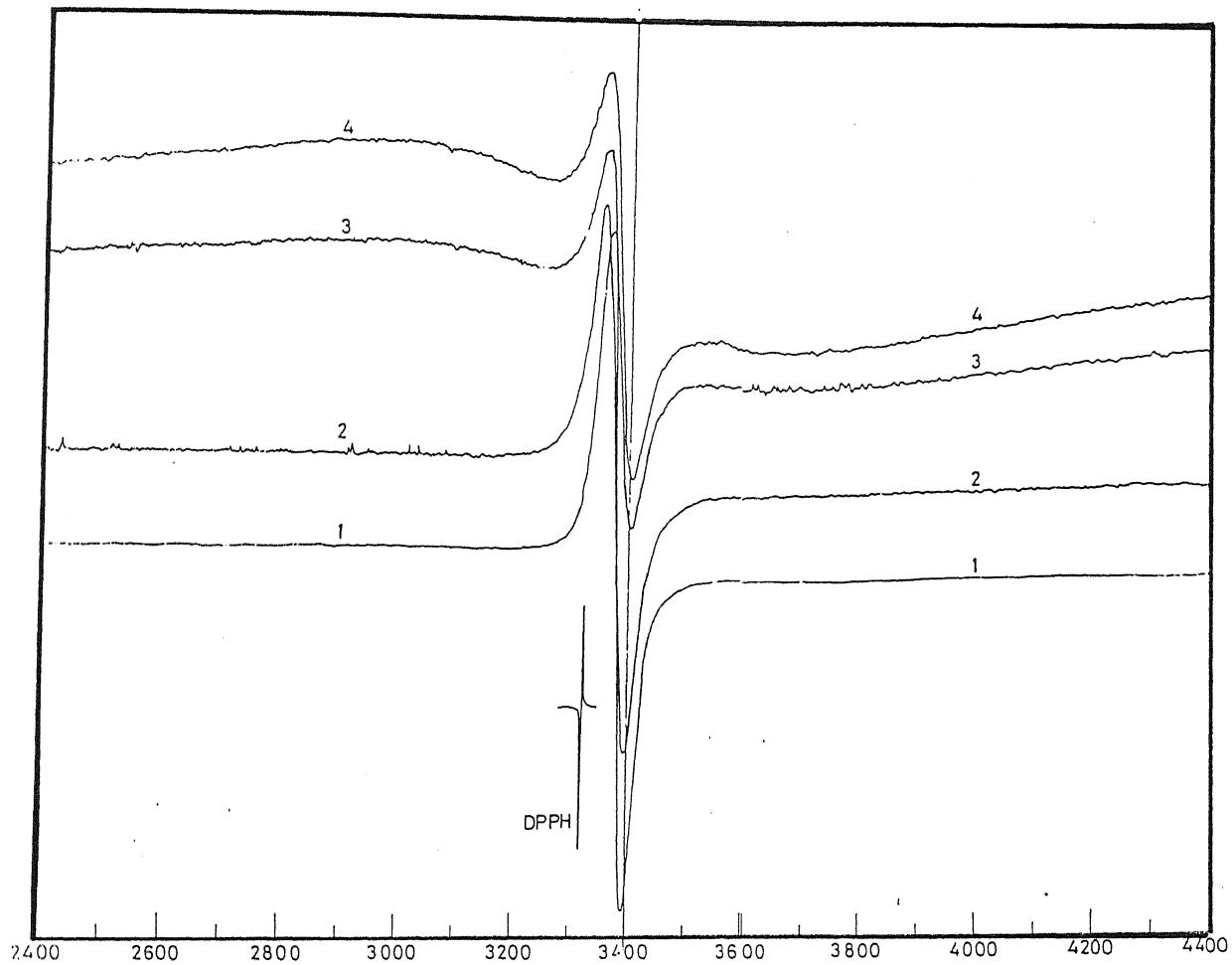


Figure 3.3 EPR Spectra of vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$
1) AlCrV_0 2) $\text{AlCrV}_{0.5}$ 3) $\text{AlCrV}_{1.0}$ 4) $\text{AlCrV}_{1.5}$

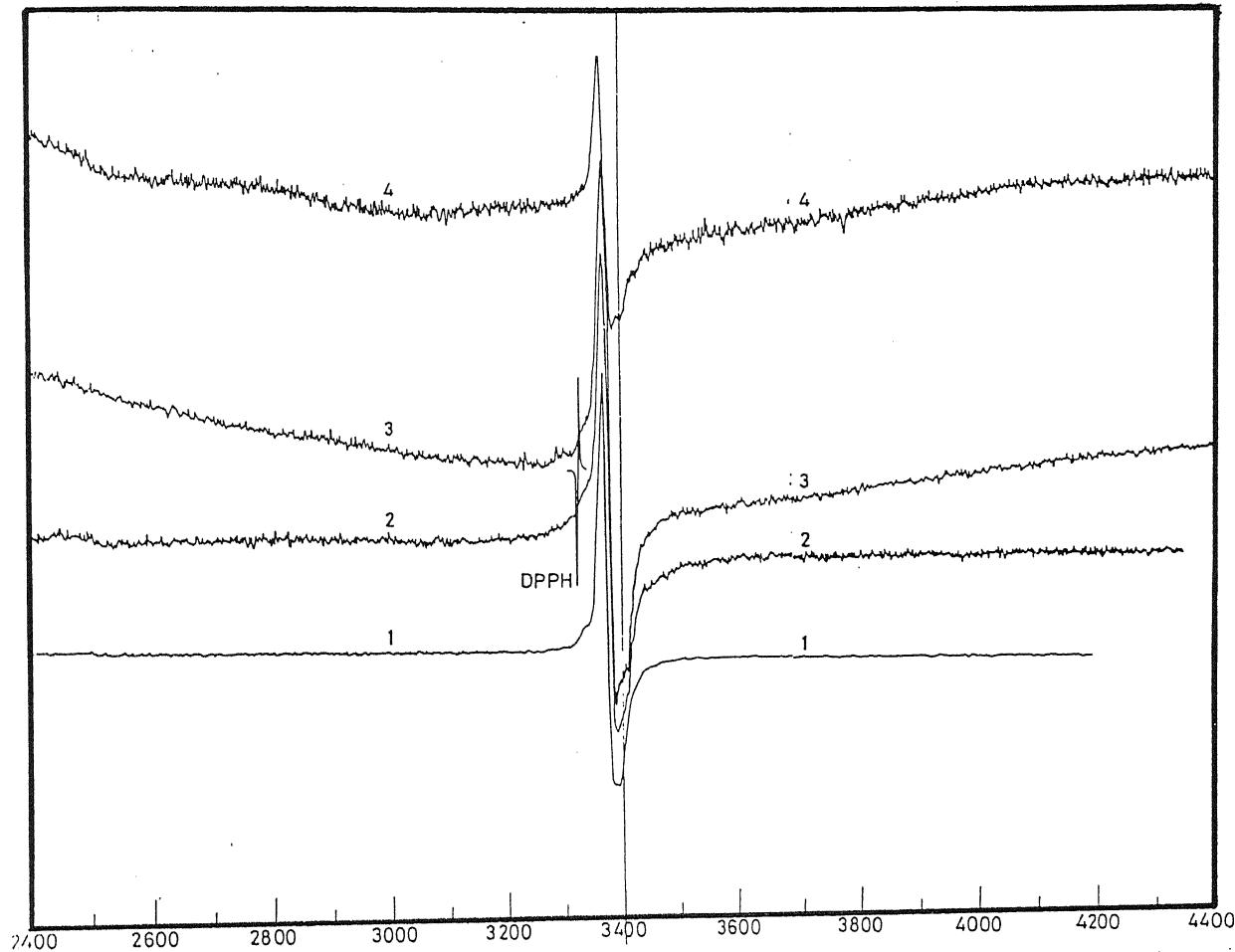


Figure 3.4 EPR Spectra of vanadium oxide modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$
1) TiCrV_0 2) $\text{TiCrV}_{0.5}$ 3) $\text{TiCrV}_{1.0}$ 4) $\text{TiCrV}_{1.5}$

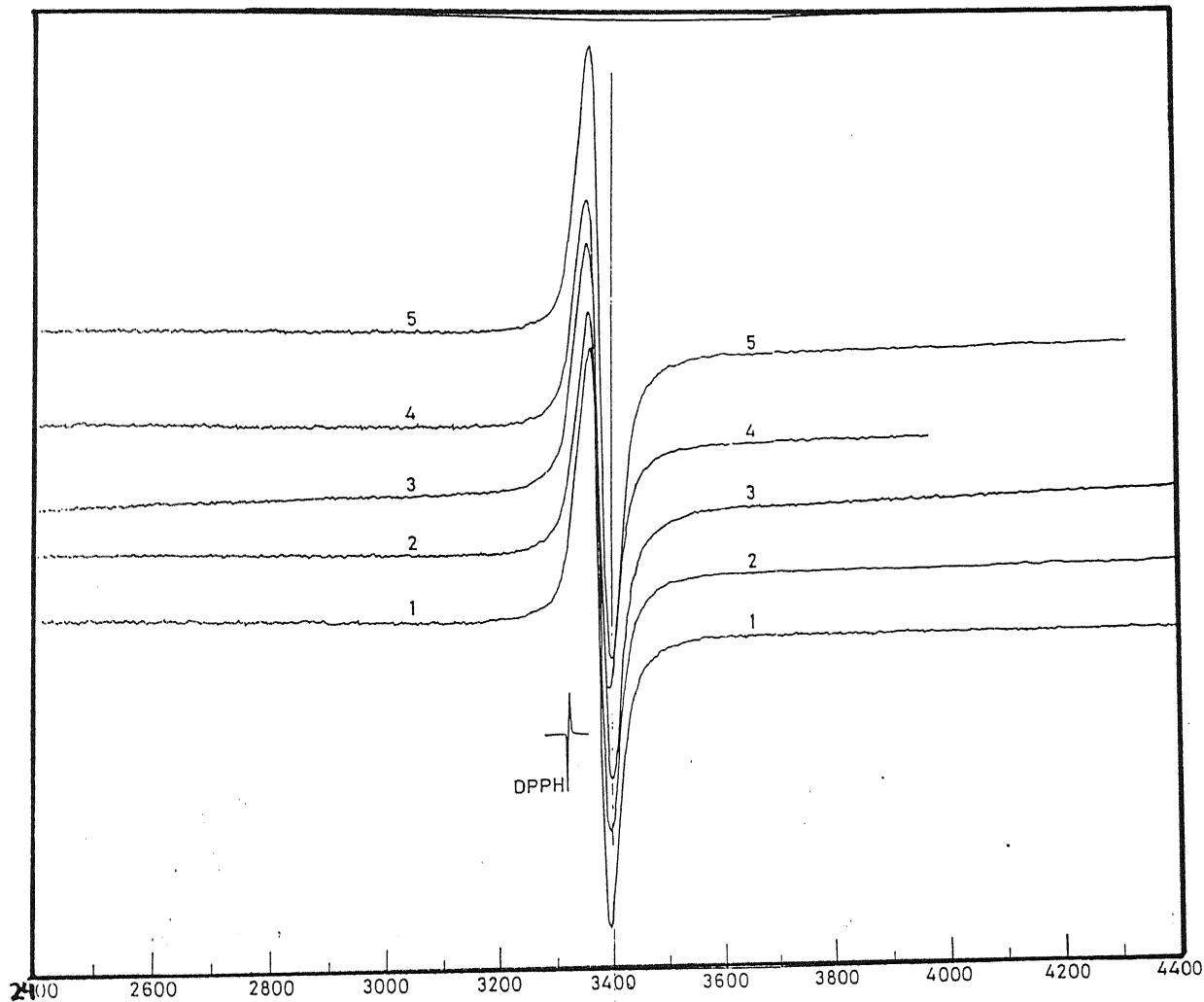


Figure 3.5

EPR Spectra of Sodium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts

1) AlCrNa_0 2) $\text{AlCrNa}_{0.02}$ 3) $\text{AlCrNa}_{0.06}$ 4) $\text{AlCrNa}_{0.1}$ 5) $\text{AlCrNa}_{0.15}$

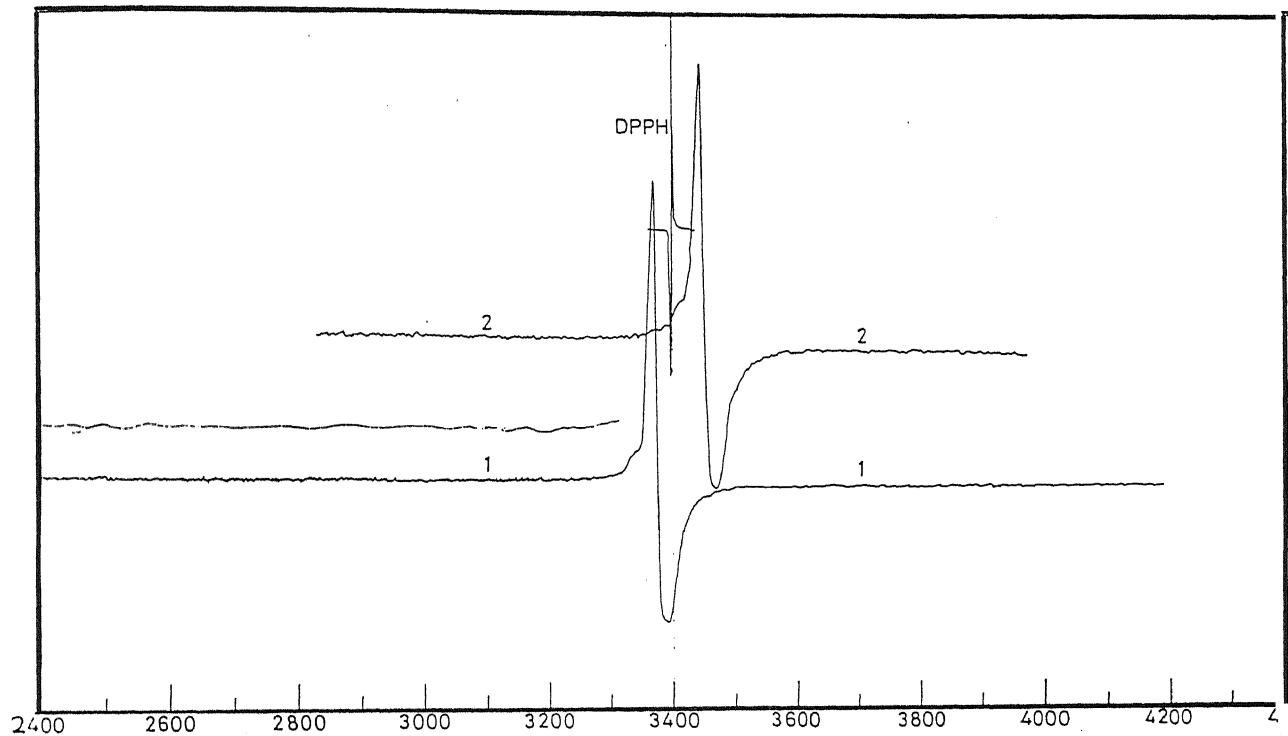


Figure 3.6

EPR Spectra of Sodium modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts

1) TiCrNa_0 2) $\text{TiCrNa}_{0.06}$

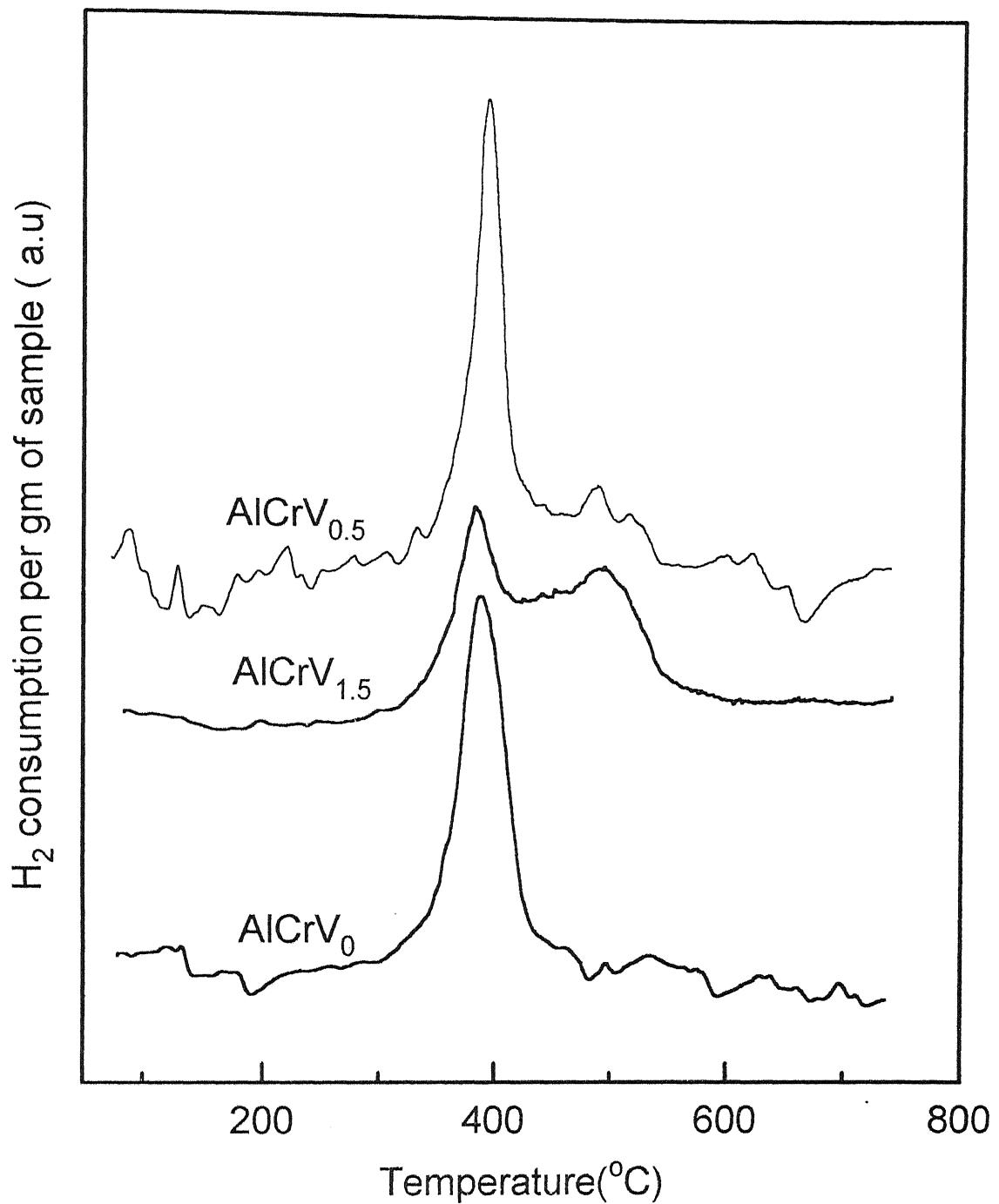


Figure 3.7 TPR plot of the 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts modified with vanadium oxide

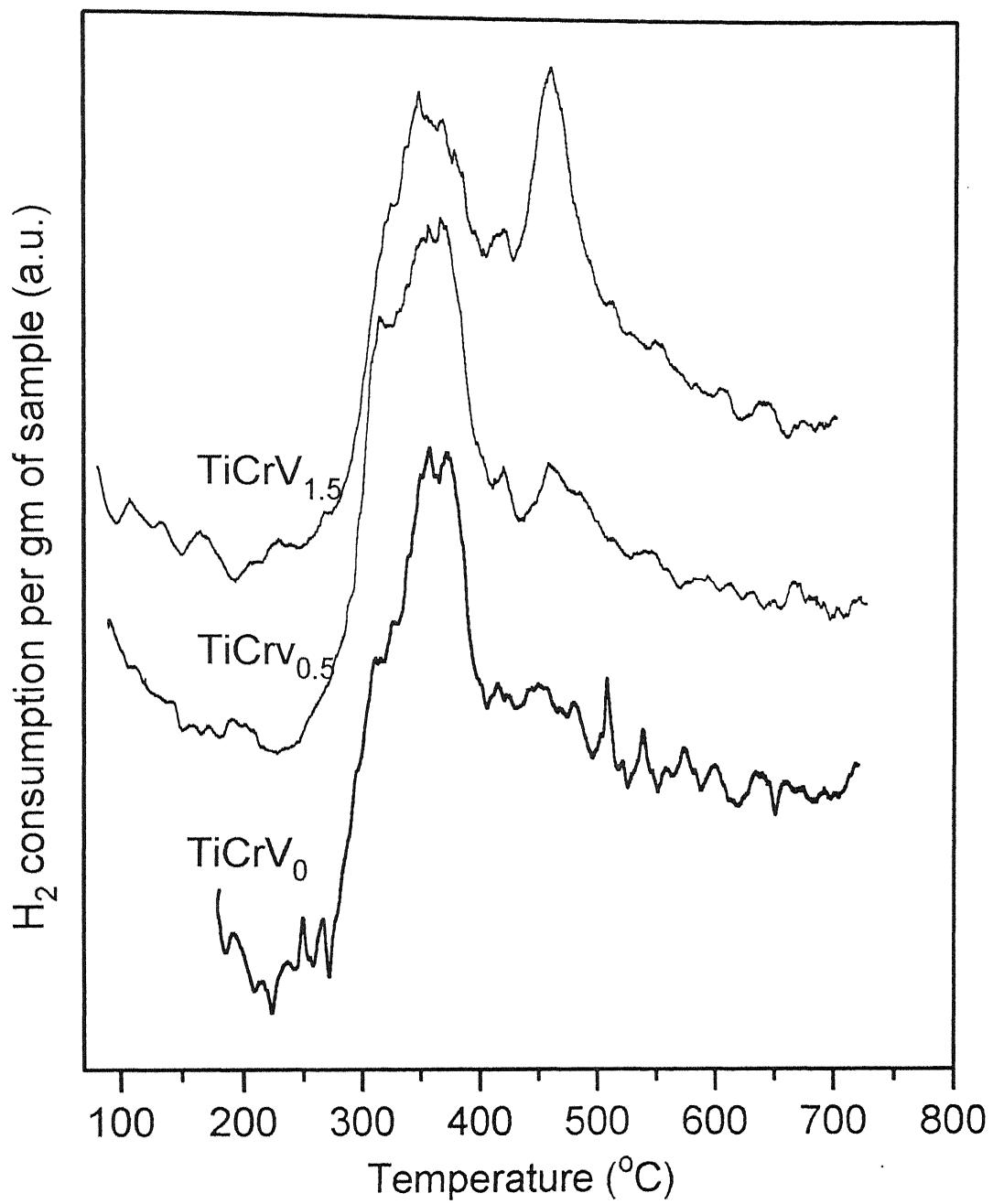


Figure 3.8

TPR plot of the 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts modified with vanadium oxide

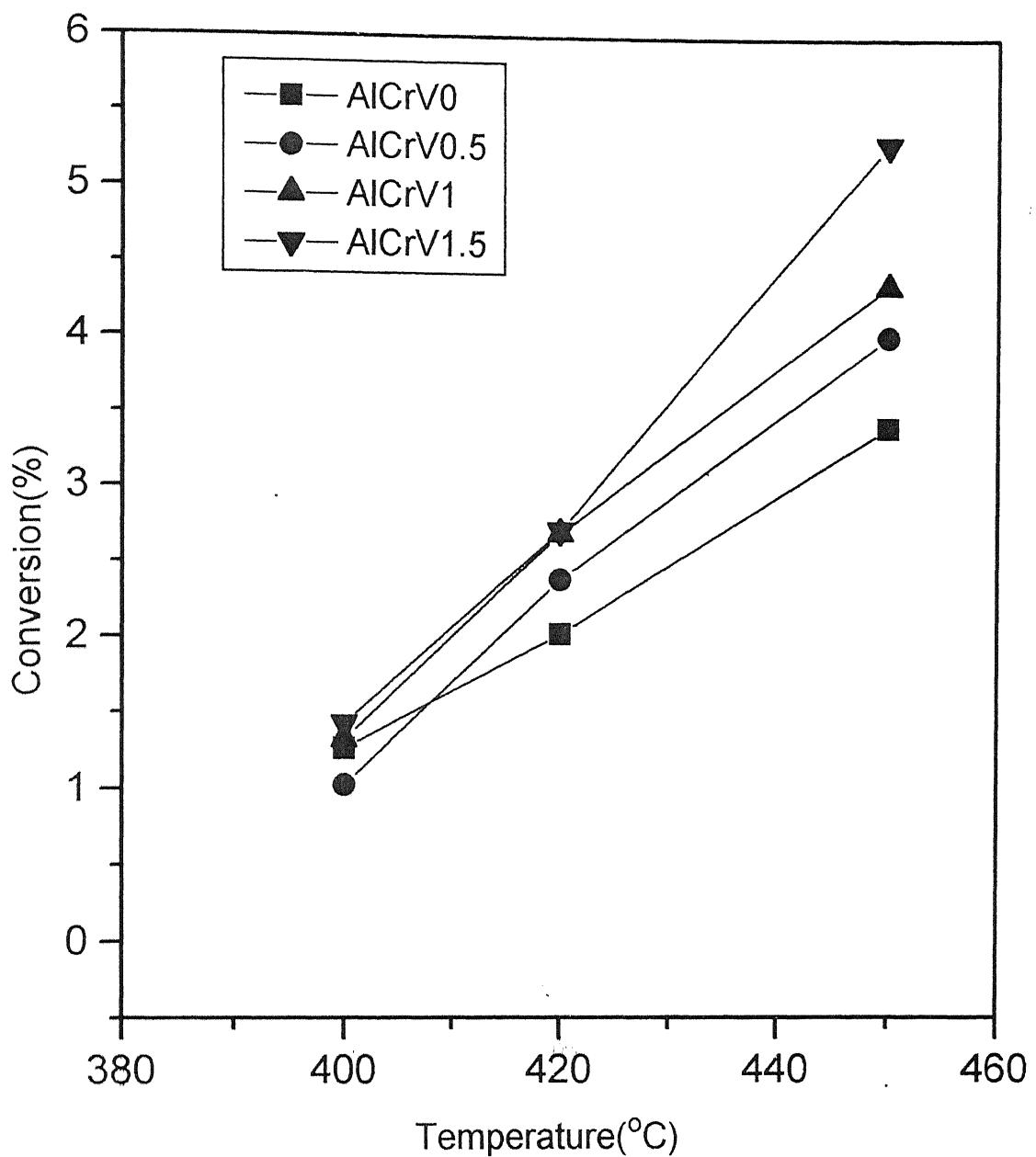


Figure 3.9 Variation of propane conversion with temperature for 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts modified with various amount of vanadium oxide

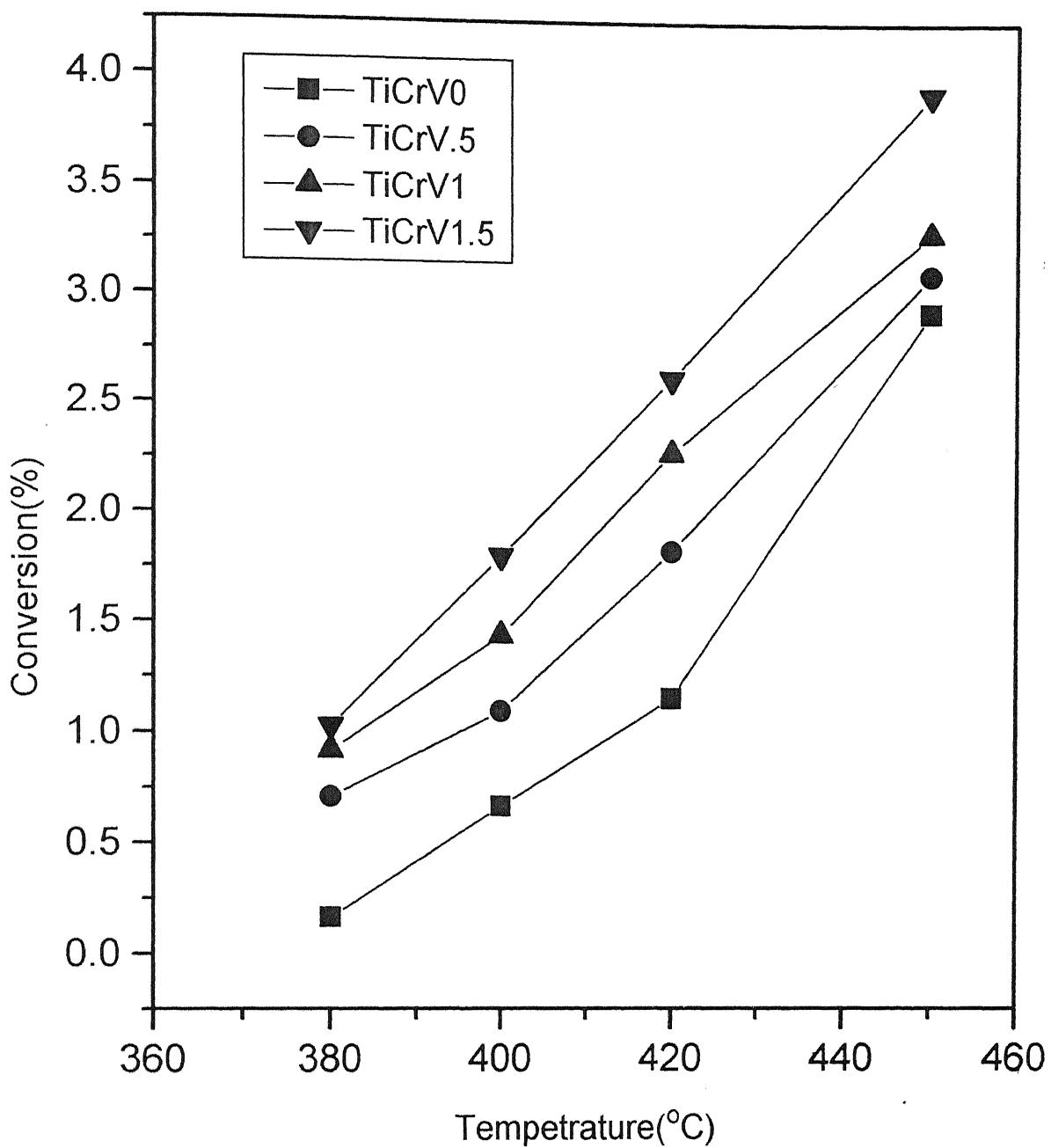


Figure 3.10 Variation of propane conversion with temperature for 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts modified with various amount of vanadium oxide

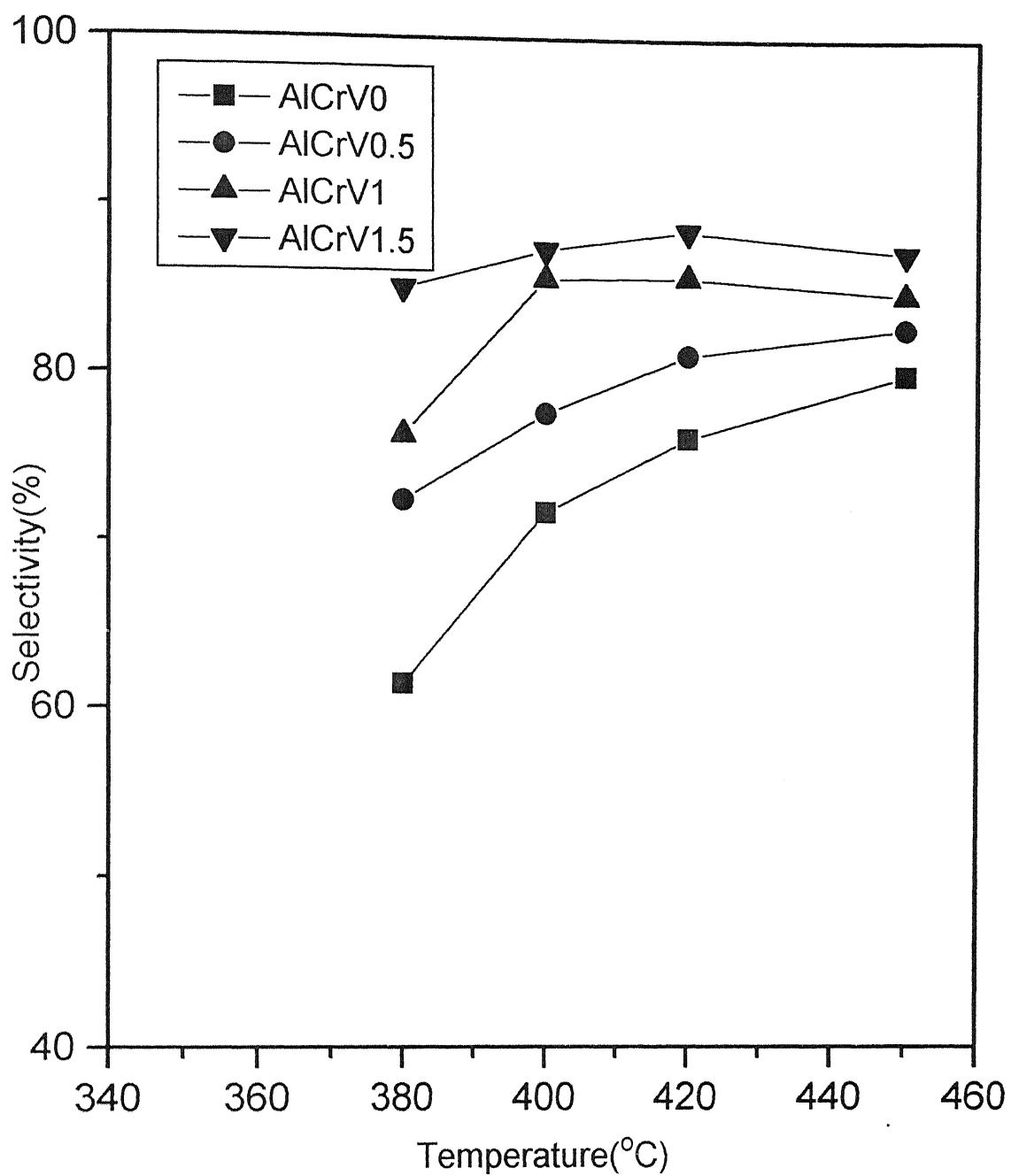


Figure 3.11 Variation of propene selectivity with temperature for 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts modified with various amount of vanadium oxide

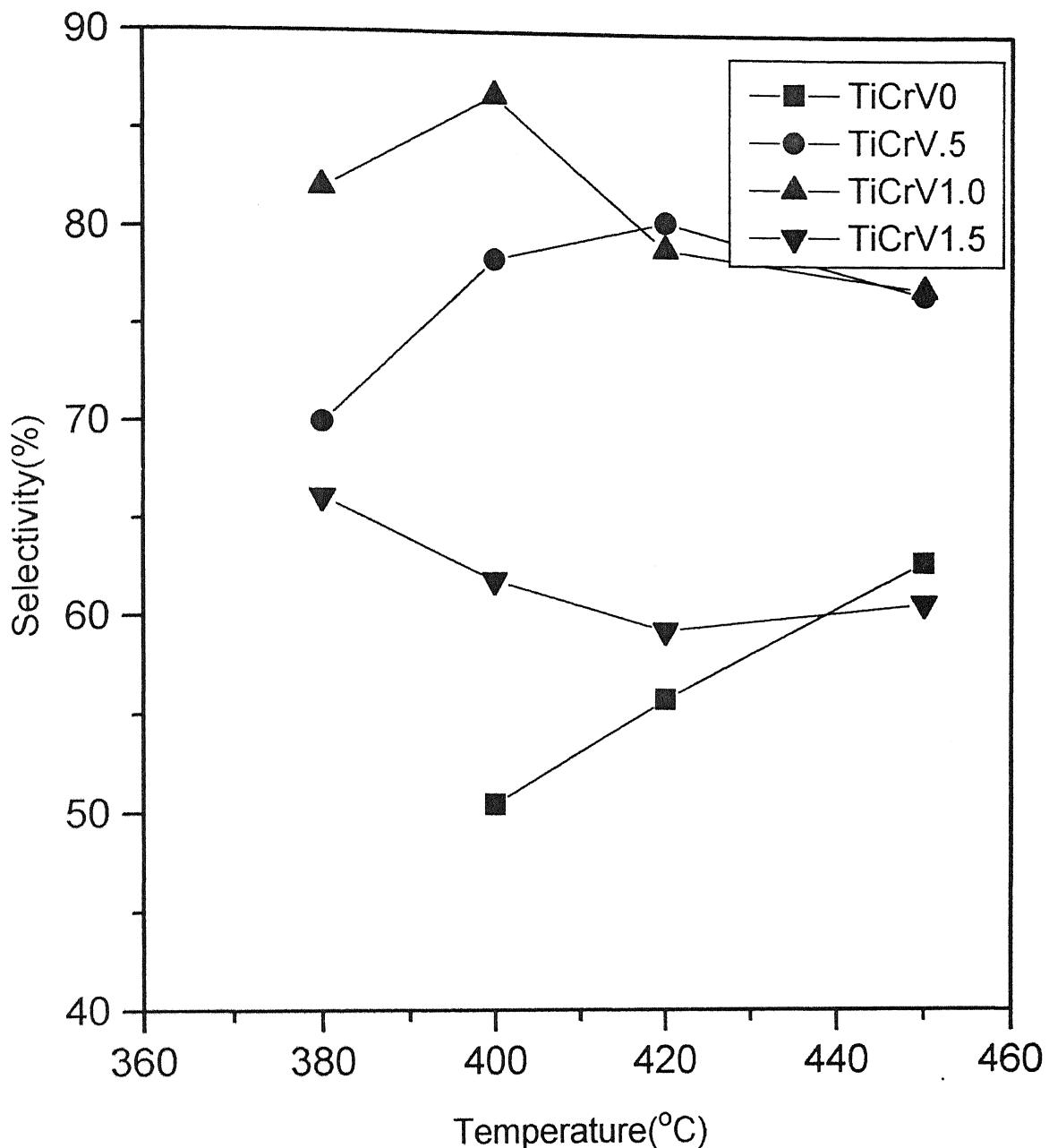


Figure 3.12 Variation of propene selectivity with temperature for 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts modified with various amount of vanadium oxide

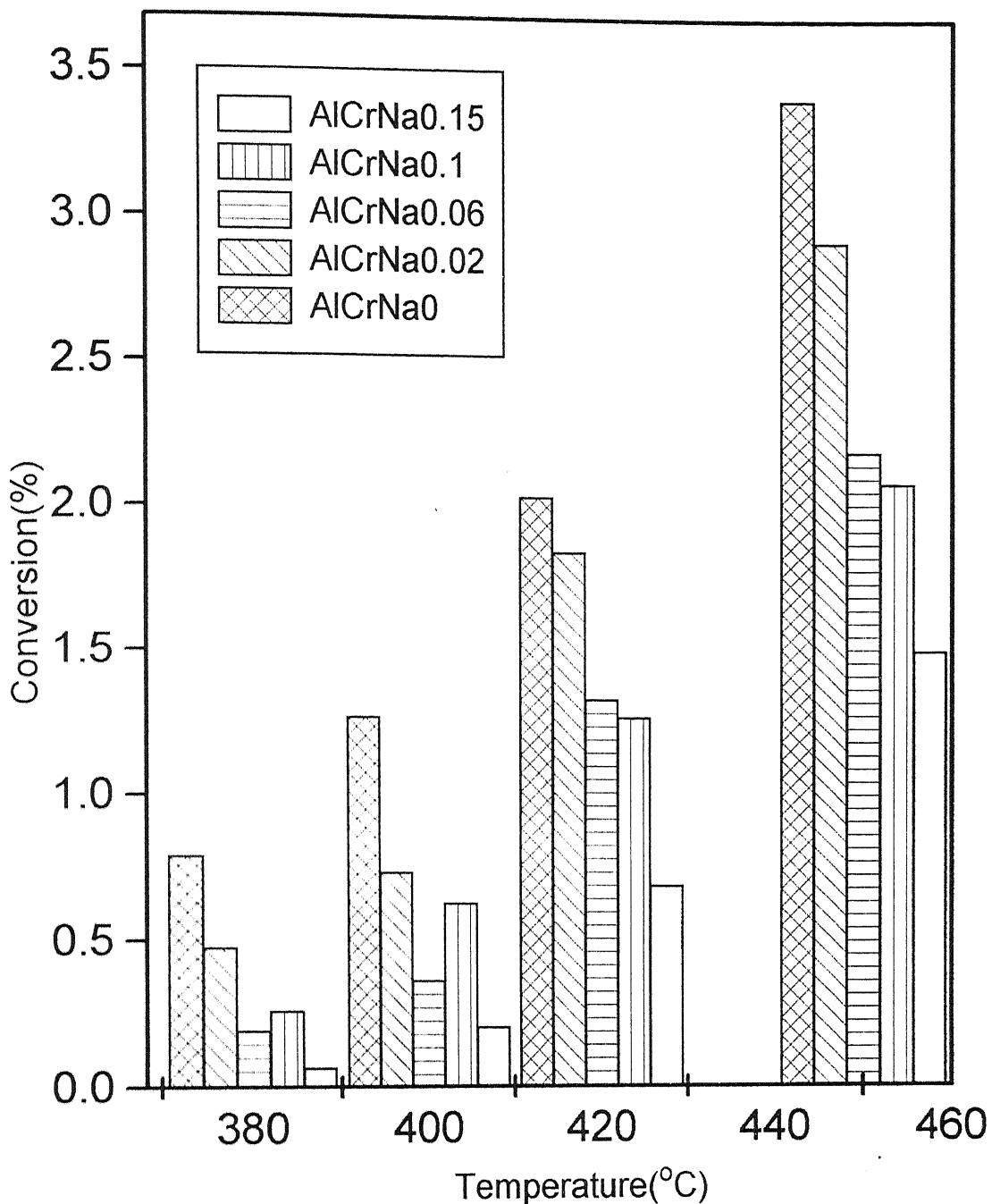


Figure 3.13 Variation of propane conversion with temperature for 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts modified with various amount of sodium

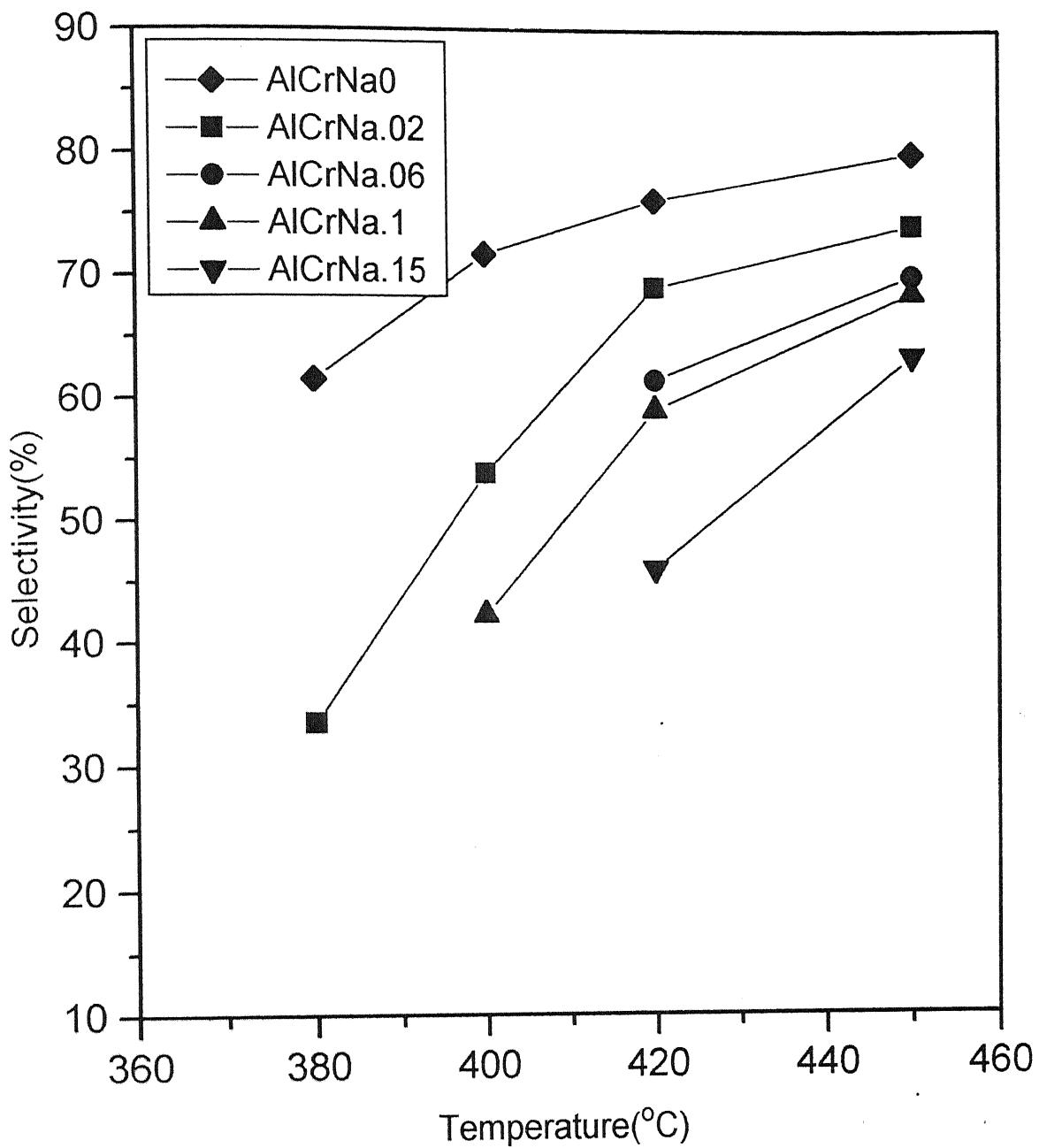


Figure 3.14 Variation of propene selectivity with temperature for 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts modified with various amount of sodium

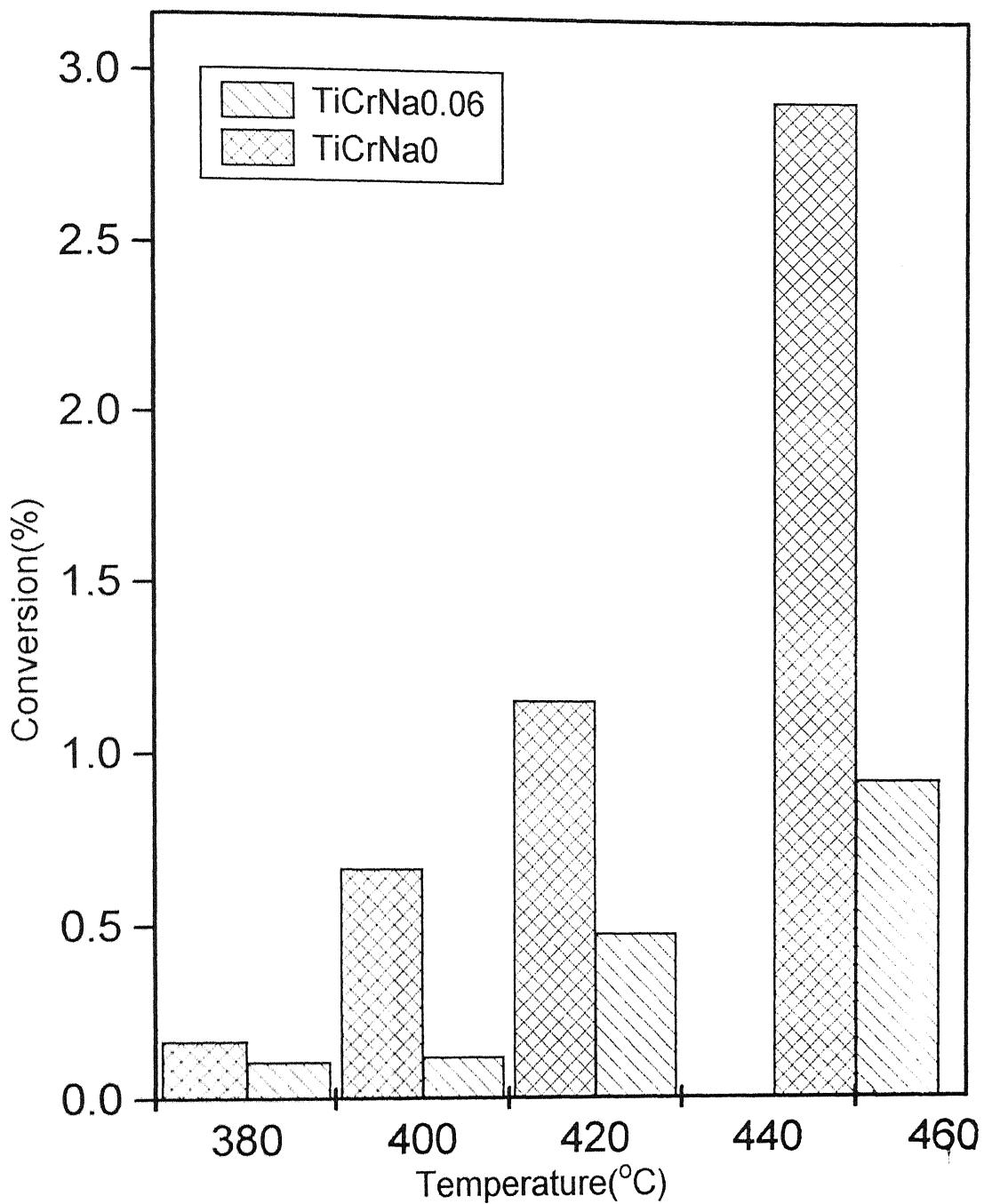


Figure 3.15 Variation of propane conversion with temperature for 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts modified with various amount of sodium

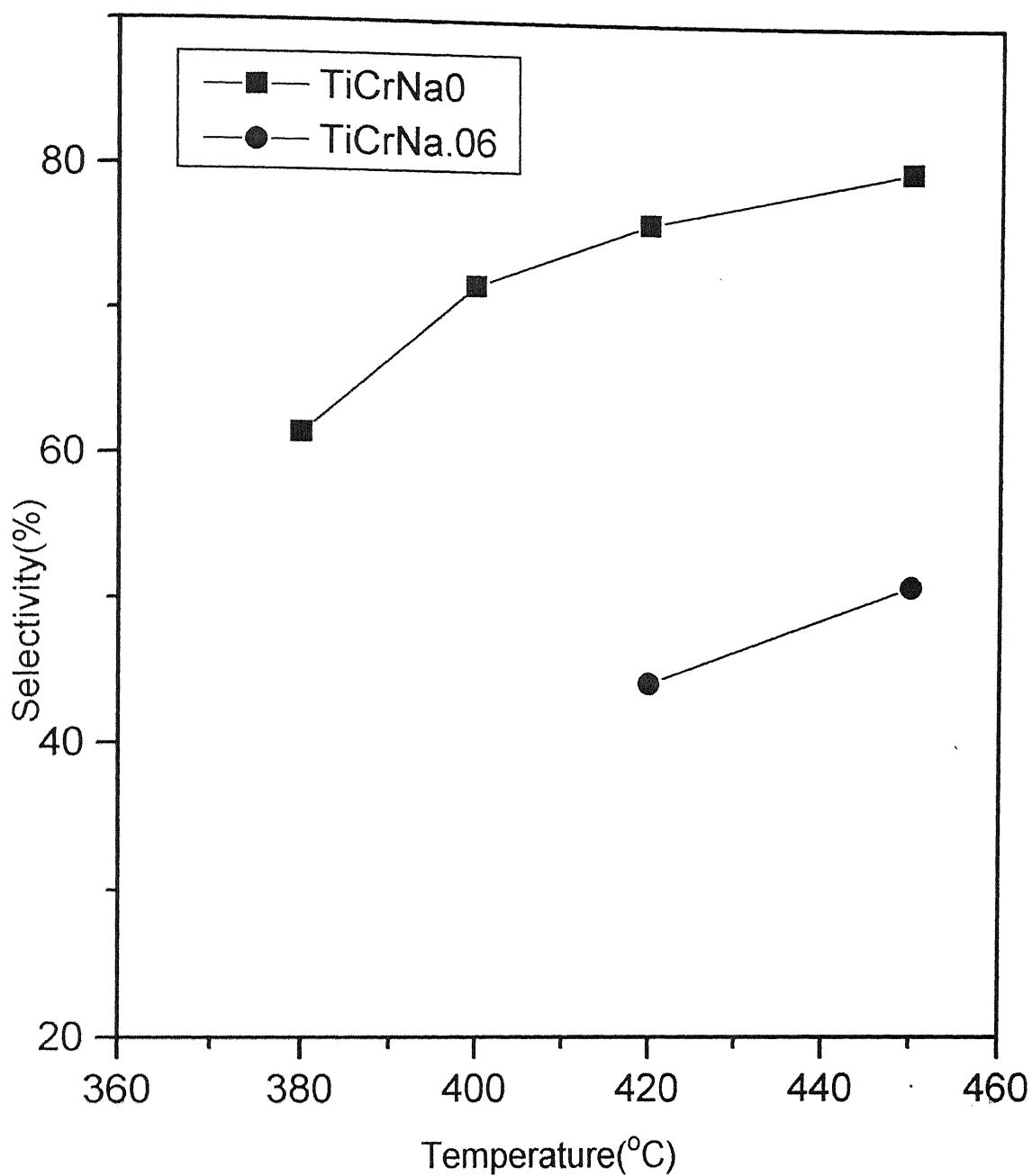


Figure 3.16 Variation of propene selectivity with temperature for 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts modified with various amount of sodium

Chapter 4

Discussion

The primary objective of the present study is to understand the effect of additives on $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts. Vanadium oxide and sodium oxide were used as model additives. Before discussing the effect of additives on supported chromium oxide catalysts it is worthwhile first to discuss about the unmodified chromium oxide catalysts supported on Al_2O_3 and TiO_2 . Cherian et al. [18] reported the influence of support and loading on these catalysts. The characterizations of the catalysts were achieved by various techniques. Raman spectra, under ambient condition, revealed that the monolayer limits for the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts were less than 15% and 4% Cr_2O_3 loading, respectively. Surface chromia species were present in these catalysts up to monolayer loadings. The presence of the surface chromium oxide species was detected by Raman spectroscopy where a band at 850 to 880 cm^{-1} was observed for the 5 to 15% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts and at 850 to 900 cm^{-1} for the 1 to 4 % $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts. UV-Vis spectroscopy results suggest that the surface chromia species was in +6 oxidation state. The amorphous surface chromia species is known to change its structure at high temperature where the surface moisture present under ambient conditions desorbs. At high temperature, dehydrated conditions, a mono-oxo chromium oxide species has been proposed to exist [10]. EPR spectra also reveal presence of Cr^{5+} species in all chromium oxide loading below monolayer coverage. Furthermore, Cr^{5+} species was shown to be chemically inactive.

Modified Chromia Catalysts

Surface Area

The BET surface area results in Table 3.1 for vanadium oxide modified chromia catalysts supported on Al_2O_3 reveal a decrease in specific surface area for the vanadium oxide modified catalysts. A large difference in the area of the support and vanadium oxide modified catalysts can be attributed to the blocking of the pores in the support with initial chromia and vanadia loading. Further addition of vanadium oxide to the sample results in small but noticeable decrease in surface area. This suggests that there is a small effect of vanadium oxide loading on the modified catalysts. For the vanadium oxide modified $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts (Table 3.2), the specific surface area were relatively constant. It appears that the chromia phase has a texture stabilizing action against the changes provoked by deposition of the vanadia phase.

The samples doped with sodium have also similar surface area (Table 3.3) as the unmodified chromium oxide supported on Al_2O_3 or TiO_2 catalysts. This may be due to the low amounts of dopants used.

XRD

XRD pattern of vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ is shown in Fig. 3.1. It revealed that no phase transformation of Al_2O_3 occurred after impregnation of chromium oxide and vanadia. This indicates that newly formed compounds were not detected because they were probably amorphous or very well dispersed on the support. Similar results for the other sodium and vanadium oxide modified catalyst were observed.

Consequently, XRD was not able to provide additional information about the sodium, chromium and vanadium oxide phase.

Raman spectroscopy

Raman spectroscopy is carried out for the vanadium oxide modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts under ambient condition. The Raman spectra reveal the presence of surface chromium oxides species along with additional peaks at high vanadium oxide loading sample. These peaks at 811 cm^{-1} and 920 cm^{-1} can be assigned to the metavanadate species [35]. Since surface chromia species were present in all vanadium-loading sample it indicates that addition of vanadium did not change the surface chromia species.

EPR Spectroscopy

The literature reported several EPR studies of chromium ions dispersed on different supports [32-33]. Generally the samples exhibit three kinds of signals:

- i. A signal (denoted Υ) with EPR parameters $g = 1.97$ and $\Delta H \leq 60\text{ G}$. This signal is assigned to Cr^{5+} species in an octahedral coordination.
- ii. A positive lobe (denoted δ) with a parameter g around 4 attributed to Cr^{3+} ions in an octahedral environment.
- iii. The third signal at $g = 2-2.5$ (denoted β) with $\Delta H \leq 900\text{ G}$ was generally assigned to clustered Cr^{3+} ions.

The EPR analysis reveals the strong axially symmetric peak centered around 3400 G ($g=1.96$, $\Delta H=40-60\text{ G}$) in all the unmodified and vanadium modified samples supported on Al_2O_3 and TiO_2 (Fig 3.3 and 3.4). Previous study suggests that this peak corresponds to the Υ signal of isolated axially symmetric Cr^{5+} species as reported above. The concentration of Cr^{5+} species was observed to decrease with vanadium oxide

peak corresponds to the Υ signal of isolated axially symmetric Cr^{5+} species as reported above. The concentration of Cr^{5+} species was observed to decrease with vanadium oxide loading. The decrease in Cr^{5+} species concentration appears to be due to the presence of vanadium oxide species in both series of catalysts. Additional features due to vanadium oxide (V^{4+}) species was not observed in EPR spectra, which suggests that paramagnetic V^{+4} centres are not present. In sodium modified chromium oxide catalysts the EPR spectra reveal Cr^{5+} species only and the intensity of Cr^{5+} were nearly the same in all catalysts. It appears that the Cr^{5+} species is not being affected by sodium and may be inside the support.

Temperature Programmed Reduction Studies

Temperature programmed reduction is a valuable technique for investigating the reducibility of chromium species. In the present study hydrogen is used as the reductant. This technique involves monitoring the removal of oxygen from the catalyst surface by means of hydrogen while the temperature is increased linearly with time. The temperature at which the reduction peak maxima occur gives information about the reducibility of the catalysts. Lower the reduction peak maxima, T_{\max} , more easily is the catalysts reduced.

Unmodified catalysts on either of the support show a single reduction peak. For example, $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ show a peak at $389\text{ }^{\circ}\text{C}$ and $368\text{ }^{\circ}\text{C}$ respectively [18], and $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts show a single peak at $490\text{ }^{\circ}\text{C}$ and $460\text{ }^{\circ}\text{C}$, respectively [36]. For the vanadium oxide modified $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts two reduction peaks are observed, see Figures 3.7 and 3.8. Since the first peak ($\sim 390\text{ }^{\circ}\text{C}$ for Al_2O_3 and $360\text{ }^{\circ}\text{C}$ for TiO_2) in the modified catalysts is similar to that in

similar to the V_2O_5/Al_2O_3 and V_2O_5/TiO_2 catalysts, and these peaks are assigned to the reduction of surface vanadium oxide species. The presence of two peaks in the modified samples suggests that the reduction properties are not influenced by the other species. Thus, the reduction of the chromium and vanadium oxide species occurs independent of each other.

TPR study for sodium doped 5% Cr_2O_3/Al_2O_3 and 1% Cr_2O_3/TiO_2 catalysts also reveal a single reduction peak. However, the amount of reduction, given by the H/Cr, decreases monotonically. The decrease in H/Cr ratio with increase in sodium suggests that part of the chromium oxide species is strongly bound to sodium and does not get reduced. Previous study [21] reported the higher value of T_{max} for alkali metal doped catalysts than that of unmodified catalysts. In the present study a increase in T_{max} is also observed for sodium modified catalysts. The increase in T_{max} value indicates that the presence of alkali metal affects the reducibility of active species [21]. The decrease in H/Cr values in sodium-modified samples indicates the strong interaction of between sodium and chromium species.

In summary, the surface area and XRD patterns suggest that modification of the supported chromium oxide catalysts do not affect the support structure. Raman studies reveal that surface vanadium and chromium oxide phases are present on the oxide support. Furthermore, TPR studies reveal that the surface chromium and vanadium oxide species appear not to interact with each other. However, sodium appears to interact strongly with the surface chromium oxide phase.

Chemical Reactivity Studies

Cherian et al. [18] reported the ODH activity for unmodified chromia catalysts supported over Al_2O_3 and TiO_2 . The reactivity studies revealed that the activity and selectivity of the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts depends upon the type of chromium oxide species present. The maximum conversion was observed for the 15 % $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 4 % $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalyst. At these loadings the physical characterization studies reveal that the maximum amount of surface chromia species are present. The activation energies for the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts were similar suggesting that the reaction mechanism were similar. The smaller value for activation energy for bulk Cr_2O_3 suggests that a different rate- determining step is involved. Furthermore, the turnover frequency, TOF, of the surface chromium oxide species on TiO_2 was greater than on Al_2O_3 .

Catalytic activity and selectivity results at steady state for vanadium-modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts are shown in Fig. 3.9 to Fig 3.12. Propene and carbon oxides were the only reaction products detected. Since equal amounts of catalysts were tested for the ODH reaction, the conversion values observed are proportional to the activity. The activity increases as the V/Cr ratio increases for both series of catalysts sample supported over Al_2O_3 and TiO_2 . The Raman spectra and TPR studies of vanadium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ indicate that the addition of vanadium oxide does not affect the chromium oxide species since the Raman spectra and TPR profiles reveal combination of individual components. This result is in agreement with results reported previously in literature [12]. Surface vanadium oxide species is known also to be active for the ODH of propane [35]. Consequently, addition of vanadium to the supported chromium oxide catalysts results in an increase in ODH

activity. The cumulative nature of the activities for the surface chromium and vanadium oxide species is, observed since the conversion of the vanadium modified $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts is within 20 % of the conversion that would be obtained by the addition of the individual catalysts, i.e., $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3 + \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ or $\text{Cr}_2\text{O}_3/\text{TiO}_2 + \text{V}_2\text{O}_5/\text{TiO}_2$. The cumulative nature is, however, not observed for the vanadium oxide modified $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts. The conversion of the vanadium oxide modified $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts is less than the conversion that would be obtained by the individual components, i.e., $\text{Cr}_2\text{O}_3/\text{TiO}_2 + \text{V}_2\text{O}_5/\text{TiO}_2$. The decrease in conversion may be due to mass and heat transfer effects since the activation energies for the vanadium modified catalysts are less than 80 kJ/mol range compared to 100 to 120 kJ/mol that is expected.

The propene selectivity of the vanadium modified $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts increases as vanadium is added. Addition of vanadium results in a decrease in the amount of exposed surface of the oxide support. The oxide support is known to degrade propene to carbon oxides [18]. Thus, with the increase in the amount of vanadium oxide the propene selectivity increases. Since the amount of exposed support surface decreases.

The activity and propene selectivity on sodium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$, shown in Figs. 3.13 to 3.16 reveal that for all the sodium-modified catalyst tested, the activity and selectivity decreased monotonically with an increase in sodium content. From TPR studies it was observed that addition of sodium decreases the H/Cr ratio. The decrease in H/Cr is due to the poisoning of the reducible surface chromium oxide sites. Furthermore, it has been proposed that alkali doping (potassium) decreases the Lewis acidity of the catalysts [30], which decreases the

propane adsorption and consequently, conversion. In the present study the Lewis acid sites of the supports were not studied. However, poisoning of the surface chromium oxide sites appears to be the reason for the decrease in activity of the sodium modified $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts. Moreover, the decrease in conversion for sodium modified 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts was higher ($\sim 68\%$) than that of the sodium modified 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ($\sim 35\%$) despite the slightly higher coverage of the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample. It appears that the dispersion of sodium on Al_2O_3 is greater than on TiO_2 .

Selectivity to ODH product depends on both the acid-base character of catalysts and the length of fed alkane. It is not been clarified yet how the alkali metals affect the alkene selectivity, either by blocking the selective strong acid sites that favor the formation of propene and/or by blocking the propane adsorption centers. From our results it is not possible to indicate the correct mechanism that occurs during sodium modification.

In summary, ODH of propane over modified $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts indicates that the activity increases with addition of vanadium oxide to unmodified $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts. The characterization studies suggest that the surface chromium and vanadium oxide sites are independent of each other. Consequently, it appears that vanadium oxide forms a non-interacting species to the surface chromium sites and vice versa. The increase in activity is due to the presence of two different active sites. Modification of the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalysts with sodium suggest that surface chromium active centers are poisoned. Poisoning of the active sites leads to a decrease in the degree of reduction (H/Cr less), reducibility (T_{\max} higher) and ODH activity. Thus, sodium acts as an interacting additive.

Chapter 5

Conclusions

The effect of various amounts of additives (oxides of vanadium and sodium) on the structure and reactivity of the surface chromia species on low loading 5% $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and 1% $\text{Cr}_2\text{O}_3/\text{TiO}_2$ samples were successfully studied by various characterization techniques (BET, XRD, Raman, EPR and TPR) and the ODH of propane.

From the XRD analysis, no crystalline phase of V_2O_5 , Na_2O , Cr_2O_3 or combination of these were detected in the modified catalysts sample. Furthermore, the support features are also unaffected. The results of ambient Raman spectrum and TPR studies suggested that there are two types of interaction between the additives and the surface chromium oxide species. Vanadium oxide appears to directly bind to the oxide support and not significantly affecting the structure of the surface chromium oxide species. Sodium, however, appears to binds to the surface chromium oxide species by directly coordinating to it. The two types of modified catalysts also respond differently for the ODH of propane reaction. The conversion and selectivity increased with vanadium content at all temperature for the vanadium oxide modified catalysts. On the other hand, the conversion and selectivity decreased for the sodium modified catalysts. Thus, vanadium and chromium oxide form non-interacting surface species, whereas, sodium and chromium oxide form interacting species on the oxide support.

Recommendations

Based on the observations and conclusions of the present study, the following recommendations can be made:

1. More detailed characterization of the modified catalysts using techniques like XPS, DRS, dehydrated Raman spectroscopy, electron microscopy should be carried out to obtain better insight into the nature of the catalysts.
2. Effect of other additives, such as WO_3 , SiO_2 , K_2O , P_2O_5 can be studied on low loading chromium oxide catalysts supported on various pure supports.
3. Preparation of the modified catalysts should be in various sequences, i.e., deposition of the active species to the additive-support or deposition of the additive to the supported catalysts in order to obtain the effect of preparation sequence on the structure- reactivity of the modified catalysts.
4. Reaction study should be carried out at different propane/oxygen ratios to obtain the optimum conversion and selectivity values for various catalysts.

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APPENDIX 1

Table A1 Data for propane conversion over vanadium modified 5% Cr₂O₃/Al₂O₃

Temp. (°C)	V/Cr=0	V/Cr=0.5	V/Cr=1.0	V/Cr=1.5
350	0.13	0.1	0.15	0.53
380	0.79	0.89	1.13	1.14
400	1.27	1.03	1.33	1.43
420	2.03	2.39	2.7	2.72
450	3.41	4.01	4.35	5.3

Table A2 Data for propene selectivity for vanadium modified 5% Cr₂O₃/Al₂O₃

Temp.(°C)	V/Cr=0	V/Cr=0.5	V/Cr=1.0	V/Cr=1.5
350	0	0	0	84.9
380	68.8	76.4	76.3	85.08
400	70.68	77.67	85.7	89.20
420	75.5	81.17	85.8	88.59
450	84.3	81.78	87.36	84.9

Table A3 Data for propane conversion over vanadium modified 1% Cr₂O₃/TiO₂

Temp.(°C)	V/Cr=0	V/Cr=0.5	V/Cr=1.0	V/Cr=1.5
350	0.065	0.17	0.62	0.76
380	0.167	0.71	0.92	1.03
400	0.67	1.1	1.44	1.8
420	1.16	1.83	2.28	2.62
450	2.93	2.97	3.29	3.93

Table A4 Data for propene selectivity for vanadium modified 1% Cr₂O₃/TiO₂

Temp. (°C)	V/Cr=0	V/Cr=0.5	V/Cr=1.0	V/Cr=1.5
350	0	0	80.4	66.9
380	0	70	82	66.1
400	50.5	87	81.8	61.9
420	55.9	80.4	79.0	59.4
450	62.9	76.7	77.0	60.8

Table A5 Data for propane conversion over sodium modified 5% Cr₂O₃/Al₂O₃

Temp. (°C)	Na/Cr=0	Na/Cr=0.02	Na/Cr=0.06	Na/Cr=0.1	Na/Cr=0.15
350	0.13	0.07	0.04	0.02	0.02
380	0.79	0.47	0.19	0.26	0.06
400	1.27	0.73	0.36	0.63	0.20
420	2	1.84	1.3	1.30	0.69
450	3.41	2.92	2.2	2.0	1.50

Table A6 Data for propene selectivity for sodium modified 5% Cr₂O₃/Al₂O₃

Temp. (°C)	Na/Cr=0	Na/Cr=0.02	Na/Cr=0.06	Na/Cr=0.1	Na/Cr=0.15
350	0	0	0	0	0
380	61.5	33.6	0	0	0
400	71.75	53.9	0	42.3	0
420	76.2	69	59.5	59	46.1
450	80	74	70	69.6	63.4

Table A7 Data for propene yield for vanadium modified 5% Cr₂O₃/Al₂O₃

Temp. (°C)	V/Cr=0	V/Cr=0.5	V/Cr=1.0	V/Cr=1.5
350	0	0	0	0.45
380	0.62	0.68	1.0	0.98
400	0.82	0.80	1.14	1.25
420	1.51	1.94	2.32	2.33
450	3.37	3.28	3.8	4.5

Table A8 Data for propene yield for vanadium modified 1% Cr₂O₃/TiO₂

Temp. (°C)	V/Cr=0	V/Cr=0.5	V/Cr=1.0	V/Cr=1.5
350	0	0	0.49	0.30
380	0	0.49	0.76	0.68
400	0.34	0.95	1.47	1.12
420	0.64	1.48	1.80	1.55
450	1.84	2.28	2.53	2.38

APPENDIX 2

Table B1 Activation Energy values for 1% Cr₂O₃/ TiO₂ catalysts modified with various amount of vanadium

Catalysts	Overall Activation Energy (kJ/mol)	Activation Energy based on Yield (kJ/mol)
TiCrV ₀ *	120	131
TiCrV _{0.5}	80	76.6
TiCrV ₁	76	47
TiCrV _{1.5}	62.7	61

Table B2 Activation Energy values for 5% Cr₂O₃/ Al₂O₃ catalysts modified with various amount of vanadium

Catalysts	Overall Activation Energy (kJ/mol)	Activation Energy based on Yield (kJ/mol)
AlCrV ₀ *	80	114
AlCrV _{0.5}	107	111
AlCrV ₁	94	95.5
AlCrV _{1.5}	105	102.8

Table B3 Activation Energy for 5% Cr₂O₃/Al₂O₃ and 1% Cr₂O₃/ TiO₂ catalysts modified with various amount of sodium

Catalysts	Overall Activation Energy (kJ/mol)	Activation Energy based on Yield (kJ/mol)
AlCrNa ₀	79	87.6
AlCrNa _{0.02}	109	135
AlCrNa _{0.06}	141	45.6
AlCrNa _{0.1}	91	133
AlCrNa _{0.15}	160	221
TiCrNa _{0.06}	160	110